PB87-132809

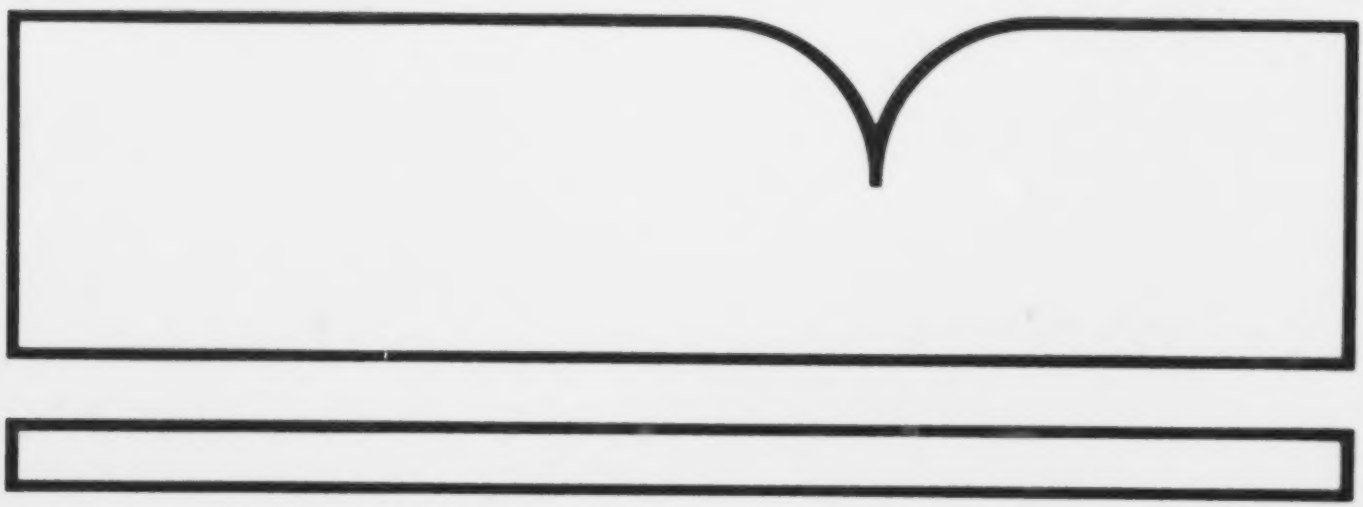
Standardization of EPA (Environmental Protection Agency) Method 8610, Part 2

Battelle Columbus Div., OH

Prepared for

Environmental Monitoring and Support Lab.-Cincinnati, OH

Dec 86



U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-132809

EPA/600/4-86/038
December 1986

REVISED FINAL REPORT

on

STANDARDIZATION OF EPA METHOD 8610, PART 2

by

S. V. Lucas, A. Riggin, T. F. Cole, and W. M. Cooke
Battelle Columbus Division
Columbus, Ohio 43201-2693

Contract Number 68-03-1760
Work Assignment 10

Project Officer

Fred K. Kawahara
Physical and Chemical Methods Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/4-86/038	2.
3. RECIPIENT'S ACCESSION NO. PB87 132809/AS	
4. TITLE AND SUBTITLE Standardization of EPA Method 3610, Part 2	5. REPORT DATE December 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) S. V. Lucas, A. Riggin, T. F. Cole, W. M. Cooke	8. PERFORMING ORGANIZATION REPORT NO
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Columbus Division Columbus, Ohio 43201-2693	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. 68-03-1760 Work Assignment #10 (continued)
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Environmental Monitoring & Support Laboratory 26 West St. Clair Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final Report 1984-1985
	14. SPONSORING AGENCY CODE EPA 600/06
15. SUPPLEMENTARY NOTES Part 1: Standardization of EPA Method 8610, EPA/600/4-85/052	

16. ABSTRACT

U.S. EPA Method 8610, "Total Aromatic by Ultraviolet Absorption" was evaluated in conjunction with U.S. EPA Method 3560, "Reverse Phase Cartridge Extraction" for the separation and semi-quantitative determination of visible or ultraviolet absorbing organic compounds listed in Appendix VIII of the Resource Conservation and Recovery Act (RCRA). The applicability of these methods was investigated in a variety of groundwater samples and method detection limit estimates were refined. Seven groundwater samples, supplied by ASTM Committee D-34 members, were evaluated for background UV absorbance, and duplicate sample extractions were used to simulate down-gradient versus up-gradient testing. Estimated response decision level was 0.02 absorbance units. Five Method 8610 analytes were evaluated for spike recoveries from both reagent water and a composite groundwater sample. One analyte was unstable in water. Four analytes had good total recoveries from reagent water ranging from 79 to 108 percent with standard deviations (except one analyte) ranging from 1 to 5 percent. Spike recoveries for composited groundwater were not reproducible due to a significant variability associated with the presence of finely divided (<20 micron) particulate.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 86
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

The information in this document has been funded wholly or in part by the U. S. Environmental Protection Agency under Contract Number 68-03-1760 (Work Assignment 10) to the Battelle Memorial Institute, Battelle Columbus Division, Columbus, Ohio 43201. It has been subject to the Agency's peer and administrative review and approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, Ohio conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report presents the results of the continuation of the evaluation of U.S. EPA Method 3560, "Reverse Phase Cartridge Extraction for Polar and Nonpolar Aromatics" and U.S. EPA Method 8610, "Total Aromatics by Ultraviolet Absorption."

Robert L. Booth, Director
Environmental Monitoring and
Support Laboratory
Cincinnati, Ohio

ABSTRACT

U.S. EPA Method 8610, "Total Aromatics by Ultraviolet Absorption" was evaluated in conjunction with U.S. EPA Method 3560, "Reverse Phase Cartridge Extraction" for the separation and semi-quantitative determination of visible or ultraviolet absorbing organic compounds listed in Appendix VIII of the Resource Conservation and Recovery Act (RCRA). As a result of a previous study, it was necessary to further investigate the applicability of these methods in a variety of ground-water samples and to refine method detection limit estimates.

Seven ground-water samples were supplied for this study by ASTM Committee D-34 members. These samples were evaluated for background UV absorbance, and duplicate sample extractions were used to simulate down-gradient versus up-gradient testing. An estimated positive response decision level was found to be 0.02 absorbance units. Five Method 8610 analytes were evaluated for spike recoveries from both reagent water and a composite ground-water sample. One analyte was found to be unstable in water and the elution solvents used. The remaining four analytes had good total recoveries from reagent water ranging from 79 to 108 percent with standard deviations of all but one analyte ranging from 1 to 5 percent. Spike recoveries for composited ground water were not reproducible due, apparently, to a significant variability in recovery of native UV absorbing material. The cause of the variability could not be specifically attributed to, but may have been associated with, the presence of very finely divided (<20 micron) particulate material.

CONTENTS

Foreword iii
Abstract iv
Figures. vi
Tables ix
Acknowledgment x

1. Introduction. 1
2. Conclusions 2
3. Recommendations 4
4. Experimental. 5
   - Apparatus 5
   - Reagents. 5
   - Acquisition of ground-water samples 6
   - Evaluation of matrix effects. 7
   - Evaluation of spike recoveries and method sensitivity in reagent water and composite ground water 9
5. Results and Discussion. 14
   - Evaluation of matrix effects of unspiked ground-water samples. 14
   - Evaluation of spike recoveries of reagent water 22
   - Evaluation of spike recoveries of composite ground water. 22
   - Evaluation of Method 8610 sensitivity 39
6. Quality Assurance 41

Appendices

A. UV spectra of composite ground-water spiking experiments. . . 43
B. Detection limit estimation for Method 8610 analytes 58
C. U.S. EPA Method 8610. 67
D. U.S. EPA Method 3560. 73

FIGURES

Number		Page
1	Instrument noise levels of the Cary 17 spectrophotometer (A) air versus air, (B) methanol versus methanol	15
2	Reproducibility of the UV spectra of replicates from a Method 3560 procedure blank (A) methanol eluents, (B) hexane eluents	16
3	UV spectra of methanol eluents from low background ground-water samples (A) sample A (B) sample B (C) sample C obtained with reference (a) procedure blank (b) methanol eluent of duplicate sample.	18
4	UV spectra of methanol eluents from medium background ground-water samples (A) sample D (B) sample E (C) sample F obtained with reference (a) procedure blank (b) methanol eluent of duplicate sample.	19
5	UV spectra of methanol eluents from high background ground-water sample (sample G) obtained with reference (a) procedure blank (b) methanol eluent of duplicate sample. .	20
6	UV spectra of hexane eluents from high and medium background ground water (A) sample F (B) sample G obtained with reference (a) procedure blank (b) hexane eluent of duplicate sample	21
7	UV spectra of methanol and hexane eluents from 3,3'-dichlorobenzidine spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 23 µg/L (c) 116 µg/L	25
8	UV spectra of methanol and hexane eluents from 2,4-dimethylphenol spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L	26
9	UV spectra of methanol and hexane eluents from 1,2-diphenylhydrazine spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L.	27
10	UV spectra of methanol and hexane eluents from 1,4-dichlorobenzene spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L.	28
11	UV spectra of methanol and hexane eluents from methoxychlor spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L. .	29

FIGURES

Number		Page
12	UV spectrum of 1,2-diphenylhydrazine at a concentration of 20 mg/L in reagent water after storage at room temperature for 48 hours (reagent water reference)	30
13	UV spectrum of 1,2-diphenylhydrazine at a concentration of 20 mg/L in reagent water (reagent water reference).	31
A-1	UV spectra of (Rep 1) methanol eluents for 3,3'-dichlorobenzidine spiked composite ground water: Spiking level (a) 0 µg/L (b) 20 µg/L (c) 100 µg/L.	43
A-2	UV spectra of (Rep 2) methanol eluents for 3,3'-dichlorobenzidine spiked composite ground water: Spiking level (a) 0 µg/L (b) 20 µg/L (c) 100 µg/L (d) pseudo baseline.	44
A-3	UV spectra of (Rep 3) methanol eluents for 3,3'-dichlorobenzidine spiked composite ground water: Spiking level (a) 0 µg/L (b) 20 µg/L (c) 100 µg/L.	45
A-4	UV spectra of (Rep 1) methanol eluents for 2,4-dimethylphenol spiked composite ground water: Spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L	46
A-5	UV spectra of (Rep 2) methanol eluents for 2,4-dimethylphenol spiked composite ground water: Spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L	47
A-6	UV spectra of (Rep 3) methanol eluents for 2,4-dimethylphenol spiked composite ground water: Spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L	48
A-7	UV spectra of (Rep 1) methanol eluents for 1,2-diphenylhydrazine spiked composite ground water: Spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L	49
A-8	UV spectra of (Rep 2) methanol eluents for 1,2-diphenylhydrazine spiked composite ground water: Spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L	50
A-9	UV spectra of (Rep 3) methanol eluents for 1,2-diphenylhydrazine spiked composite ground water: Spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L	51
A-10	UV spectra of (Rep 1) methanol eluents for 1,4-dichlorobenzene spiked composite ground water: Spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L	52
A-11	UV spectra of (Rep 2) methanol eluents for 1,4-dichlorobenzene spiked composite ground water: Spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L	53

FIGURES

Number		Page
A-12	UV spectra of (Rep 3) methanol eluents for 1,4-dichlorobenzene spiked composite ground water: Spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L	54
A-13	UV spectra of (Rep 1) methanol eluents for methoxychlor spiked composite ground water: Spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L	55
A-14	UV spectra of (Rep 2) methanol eluents for methoxychlor spiked composite ground water: Spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L	56
A-15	UV spectra of (Rep 3) methanol eluents for methoxychlor spiked composite ground water: Spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L	57

TABLES

Number		Page
1	Summary of reference standards procured for U.S. EPA Method 8610 evaluation.	6
2	Physical appearance and pH values of ground-water samples	7
3	Low spike levels of selected aromatic compounds in reagent water	12
4	High spike levels of selected aromatic compounds in reagent water	12
5	Recovery of modified Method 3560 of selected Method 8610 parameters spiked into reagent water at low level	23
6	Recovery of modified Method 3560 of selected Method 8610 parameters spiked into reagent water at high level.	24
7	Recovery of modified Method 3560 of selected Method 8610 parameters spiked into composite ground water at low level without baseline correction	33
8	Recovery of modified Method 3560 of selected Method 8610 parameters spiked into composite ground water at high level without baseline correction.	34
9	Recovery of modified Method 3560 of selected Method 8610 parameters spiked into composite ground water at low level quantified using pseudo baseline as necessary	35
10	Recovery of modified Method 3560 of selected Method 8610 parameters spiked into composite ground water at high level quantified using pseudo baseline as necessary	36
11	Results of daily quality assurance analysis of benzene standards by UV spectrometry.	42
B-1	Detection limit estimation for UV active polar organic compounds	58
B-2	Detection limit estimation for UV active nonpolar organic compounds	64

ACKNOWLEDGMENT

The authors acknowledge the continuing support of Mr. James E. Longbottom, U.S. EPA Program Manager, and Dr. Fred K. Kawahara, U.S. EPA Project Officer who were instrumental in helping meet the program goals and deadlines.

Ground water samples used in this study were supplied by the following ASTM D-34 committee members: Mr. Arden Ahnell of Sohio Research and Development, Dr. Mark Carter of Rocky Mountain Analytical Laboratory, Mr. Lee Dell of Dell Engineering, Dr. Larry Jackson of Western Research Institute, Mr. Lynn Lednicky of Dow Chemical Environmental Services and Ms. Marjory Rinaldo-Lee of Empire Soils Investigations. This study could not have been performed without the cooperation of these sample contributors.

We gratefully acknowledge Mr. Ray Cunningham, Mrs. Lorna Brown, and Ms. Eunice Adamany for their technical support; Dr. Robert E. Schwerzel who assisted with the literature and instrumental aspects of the program; and Ms. Karen B. Degner, Ms. M. Gayle Pakrosnis, Ms. Jean M. Green, and Ms. Karen S. Rush, all of Battelle Columbus Division, who assisted in preparation of the manuscript.

Mr. Thomas F. Cole planned and directed much of this study. Tom did not live to see it completed, but his ideas and spirit are part of all the programs he led at Battelle. Advancing our knowledge about pollution in the human environment, this gift from Tom lives on for all of us. We will long remember him as a strong friend and respected colleague.

SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has proposed an amendment (October 1, 1984 Federal Register) to its hazardous waste regulations under the Resource Conservation and Recovery Act (RCRA) consisting of a hierarchical analysis procedure (HAP) for ground-water testing. The proposed hierarchical procedure will allow hazardous waste facility operators to screen ground-water samples quickly for specific compounds using inexpensive methods, thus reducing their overall testing burden for regulated pollutants without jeopardizing environmental protection.

One of the proposed methods included in the hierarchical analysis protocol is EPA Method 8610, "Total Aromatics by Ultraviolet Absorption." When used in conjunction with EPA Method 3560, "Reverse Phase Cartridge Extraction," Method 8610 will allow operators of hazardous waste facilities to monitor ground water beneath their facilities for many regulated compounds. This screening data allows the operator to also make decisions for advanced testing.

To evaluate the usefulness of Methods 3560 and 8610, Battelle Columbus Division, under Contract Number 68-03-1760, conducted a research program to: (1) generate a data base of ultraviolet and visible spectral data for Method 8610 analytes; (2) evaluate Method 3560 for the collection and separation of polar and nonpolar Method 8610 analytes; and (3) evaluate Method 8610 for the analysis of total aromatic compounds. After the original scope of work was completed, evaluation of Methods 3560 and 8610 was continued. The continuation of this program was designed to: (1) acquire authentic ground-water samples from ASTM D-34 members; (2) evaluate matrix effects on ultraviolet determinative techniques using Method 8610; and (3) evaluate recoveries and detection limits of selected Method 8610 analytes spiked into reagent water and ground-water samples containing significant UV background.

SECTION 2

CONCLUSIONS

The data contained in this report on the continuation of the evaluation of EPA Method 3560 and 8610 support the following conclusions regarding the extraction recovery, matrix background effect, and method sensitivity when used to monitor ground-water samples.

- Method 8610 in its present form is not suitable for analyzing the tested composite ground-water sample. The tested water contained fine sediment particles which partially moved through the extraction cartridge and possibly interfered with the UV analysis. However, it was impossible to determine how the particles caused the poor reproducibility or even that it was indeed caused by some phenomenon associated with the particles.

- For reagent water, the simulated down-gradient versus up-gradient results suggest that a positive response of 0.02 absorbance units in the UV range 230 to 400 nm is sufficient to indicate down-gradient contamination. This result is four times higher than the proposed Method 8610 decision limit of 0.005 absorbance units.

- Using extraction coefficients reported in part 1 of this Final Report, 0.02 absorbance units as the positive response decision level, a 20-fold Method 3560 concentration factor, and recovery of 100 percent of an analyte in either the methanol or hexane eluent, it is estimated that only 28 percent of the Method 8610 analytes have a detection limit equal to or less than 10 µg/L and 68 percent have a detection limit equal to or less than 50 µg/L.

- Method 3560 was successful in recovering 3,3'-dichlorobenzidine, 2,4-dimethylphenol, 1,4-dichlorobenzene, and methoxychlor from reagent water with a recovery of 79 to 108 percent. The first two analytes were almost eluted with methanol and the last two analytes were partially eluted in both methanol and hexane. The data obtained from ground-water spiking appear to support the same conclusion, but the non-reproducibility of the background UV material does not allow quantitative demonstration of that conclusion.

- For ground water, the amount of methoxychlor recovered in the hexane fraction was substantially lower than that recovered in the same fraction for reagent water. The recoveries of the other nonpolar analyte, 1,4-dichlorobenzene, however, were comparable in the hexane fraction for both matrices. The cause of this unexpected result may be that methoxychlor was irreversibly bound to the particulate matter in the composited ground water.

SECTION 3

RECOMMENDATIONS

It is unlikely that any amount of method development will enable Methods 3560 and 8610 to adequately address most of the analytes assigned to them by the HAP scheme. These methods may, however, be adequate for a significant enough subset to justify further method development. If so, then the following recommendations are offered for further method development:

- The effect on accuracy and precision of including a step in Method 8610 for removing particulate, either by filtration or centrifugation, before UV determination should be investigated to determine whether or not Method 3560/8610 can actually be applied to the heterogeneous samples.

- Since the results of the previous study showed that polarity class separation with methanol and hexane elution solvents was probably not feasible, effort should be directed to identify a single elution solvent, such as ethanol, isopropanol or a mixed system, which will give high recovery for all analytes in a single elution.

- Further work to improve the present 20-fold concentration factor and thereby increase the method sensitivity will be required to obtain a useable method. For example, use of 1.0 mL UV cells, 2.0 mL of elution solvent in two 1.0 mL aliquots, and a 150 mL sample would provide approximately a 100-fold concentration factor.

- Other commercially available reverse phase sorbents should be evaluated to determine whether a particular type provides superior recovery and precision of the method analytes.

- If the cause of reproducibility problems for ground water identified in this work can be identified and eliminated, an automated Method 8610 approach using HPLC autosampler, UV detectors, and automated chromatography data system quantification should be developed since improved signal-to-noise and, therefore, lower detection limits should be possible than those demonstrated in this work using a double beam spectrophotometer.

SECTION 4

EXPERIMENTAL

APPARATUS

The following equipment was employed in this research program:

Recording UV/VIS Spectrophotometer	Cary 17 DX, wavelength range 186-3000 nm with expanded recorder range
Quartz cuvettes	1 cm^2 path, 3 mL spectrosil quartz
Solid phase extraction system	Baker-10 SPE™ system; consisting of a vacuum manifold with removable sample rack
Disposable Octadecyl extraction cartridge	Baker-10 SPE™ disposable filtration cartridges, Octadecyl (C_{18}), 6 mL, containing ~500 mg of 400 µm, 60 Å pore sorbent and 20 µm fritted polyethylene discs at inlet and outlet
Centrifuge filtration	Beckman Model TJ-6 Millex-SR, 0.5 micron Teflon disc in Swinney/-Luerlock holder with 5-mL syringe. Millipore Corp.

REAGENTS

The following reagents and chemical supplies were used in this work:

Reagent Water	Tap water, purified with the Milli-Q water purification system
Methanol	Burdick and Jackson high purity grade
Hexane	Burdick and Jackson, UV grade.

The suppliers and purity of the reference standards used in this study are presented in Table 1.

TABLE 1. SUMMARY OF REFERENCE STANDARDS PROCURED FOR U.S. EPA METHOD 8610 EVALUATION

Compound	CAS #	Supplier	Purity[a]
Nonpolar UV Compounds			
Benzene	71-43-2	Burdick & Jackson	NS[b]
Methoxychlor	72-43-5	Sigma	~98%
1,4-Dichlorobenzene	106-46-7	Aldrich	99+%
Polar UV Compounds			
3,3'-Dichlorobenzidine dihydrochloride	91-94-1	Sigma	NS
2,4-Dimethylphenol	105-67-9	Aldrich	99%
1,2-Diphenylhydrazine	122-66-7	Aldrich	97%

[a] As given by supplier

[b] NS -- not specified by supplier.

ACQUISITION OF GROUND-WATER SAMPLES

Ground-water samples were provided by seven ASTM members, as agreed upon at the October, 1984 ASTM D-34 meeting in Bal Harbour, Florida. Each member supplied a 2-L ground-water sample shipped in two 1-L sample jars. Battelle provided the sample containers and coordinated the sample acquisition. The sample containers were solvent rinsed, heated to 400°C in a muffle furnace, and fitted with Teflon-lined screw-caps. All samples were logged-in on

receipt and stored in a 4°C refrigerator. The date of sample receipt, pH values and the physical appearance of these samples are presented in Table 2.

TABLE 2. PHYSICAL APPEARANCE AND pH VALUES OF GROUND-WATER SAMPLES

Sample	Date Received	Physical Appearance	pH
A	2/13/85	Clear liquid, no apparent particles	7.4
B	2/21/85	Clear liquid, no apparent particles	7.8
C	2/13/85	Clear liquid, a few yellowish settled particles	7.1
D	2/06/85	Clear liquid, a few settled particles	7.6
E	2/04/85	Clear liquid, no apparent particles	6.6
F	3/02/85	Clear liquid, heavy sediment of fine particles, top layer beige color, bottom layer brown	6.8
G	3/10/85	Clear liquid, yellowish brown sediment	7.4

EVALUATION OF MATRIX EFFECTS

The reverse phase cartridge extraction procedure using EPA Method 3560 was evaluated for its ability to identify polar and nonpolar ultraviolet absorbing aromatics in ground-water samples. Under this subtask, instrument background was evaluated and the UV absorbance of the unspiked ground-water samples was investigated. A composite ground-water sample which provided significant UV background was prepared for spiking experiments.

Conditions for UV Spectrum Acquisition and Evaluation of Instrument Noise Level

A Cary 17 DX Recording Spectrophotometer equipped with both deuterium and tungsten sources was used to collect UV spectra in this and subsequent experiments. The light intensity was kept constant using the variable slit mode. Spectra were collected at a scan speed of 1 nm/sec and recorded on chart paper at a chart speed of 30 nm/inch. Spectra were acquired in the expanded absorbance range mode (0.00 to 0.20 absorbance unit full scale), unless otherwise specified. The Cary 17 DX was evaluated for noise level and baseline flatness using air versus air and solvent versus solvent. Reversing the cells had no effect on the baseline between 200 to 400 nm. Nevertheless, in all subsequent work the same cells were used for sample and reference with the same orientation regarding the UV beam incident face.

Cartridge Cleanup, Aqueous Sample Extraction and Solvent Elution Procedure

As recommended in the original task, EPA Method 3560 with the modified cartridge cleanup and solvent elution scheme was employed in this and all subsequent experiments using a "Baker-10" Solid Phase Extraction (SPE) system consisting of a vacuum manifold with removable sample rack and disposable 6-mL Octadecyl (C_{18}) columns. Adequate vacuum for sample preparation was obtained from a water aspirator. A "T" joint was installed between the vacuum source and the trap with an air bleed valve to regulate the vacuum, a vacuum gauge, and a three-way stopcock connected between the trap and the manifold to conveniently release vacuum on the vacuum manifold.

Duplicate 6-mL disposable C_{18} columns were washed first with 5 mL hexane, then with 5 mL methanol and finally with 10 mL of reagent water. The liquid flow was controlled at 5 mL/min and the vacuum was disconnected before the solution had been totally aspirated through the column to prevent the column from drying. Two 50-mL portions of ground-water sample were then aspirated through each column at a rate of 10 mL/min followed by 10 mL of reagent water. After the extraction columns were air dried under vacuum for five minutes, they were eluted with 5 mL of methanol followed by 5 mL of hexane at a rate of 5 mL/min. The vacuum was raised after each solvent

elution to eliminate interstitial solvent with more thorough drying between methanol and hexane. Both methanol and hexane column eluates were collected.

Evaluation of Cartridge Cleanup

This revised column cleanup and solvent elution procedure was evaluated for its effectiveness to provide a clean and reproducible UV background using the Cary 17 DX scanning spectrophotometer. The UV spectra were acquired in the expanded absorbance range mode (0.00 to 0.20 absorbance unit full scale). Replicates of procedure blanks were prepared by extracting blank reagent water. The UV spectra of the procedure blanks were determined for the UV range 200 to 400 nm, using one of the replicates as reference.

Investigation of Matrix Effects

Each ground-water sample was thoroughly shaken by hand to achieve a homogenous suspension before sampling. From each ground-water sample, duplicate 100-mL aliquots were taken for the matrix effects investigation.

Replicates of the procedure blank were prepared by extracting two 50-mL portions of reagent water. The UV absorbance in the 220 to 400 nm range was determined for each sample. For the background study, the UV spectrum was determined for each of the two replicates of the sample eluent versus the procedure blank, and then remeasured with sample eluent replicate 1 versus replicate 2 to provide a simulated down-gradient versus up-gradient situation.

EVALUATION OF SPIKE RECOVERIES AND METHOD SENSITIVITY IN REAGENT WATER AND COMPOSITE GROUND WATER

Spike recoveries for modified Method 3560 and sensitivity of Method 8610 were evaluated for five selected compounds at high and low spiking levels in both reagent water and composite ground-water matrices. The precision of the method was determined after triplicate extractions.

Selection of Five Representative Compounds for Spiking

Five of the 129 analytes from Method 8610 were selected for evaluation of spike recoveries and method sensitivity. Analytes which have absorption maxima between 230 to 400 nm and which encompass the range of polarities and UV sensitivities of the total method analytes were chosen. These five compounds were 3,3'-dichlorobenzidine, 2,4-dimethylphenol, 1,2-diphenylhydrazine, 1,4-dichlorobenzene, and methoxychlor.

Preparation of a Composite Ground-water Matrix

Lack of time did not allow further sampling to obtain a 5-L ground-water sample that had a medium UV background which is required for the matrix spiking experiments. Therefore, a composite sample was prepared. After reserving about 150 mL for possible future work, the remaining ~1.5-L portion of four of the ground-water samples (sample D, E, F, and G) which had the highest UV background were combined (including the sediment in each sample) in a 9-L glass bottle and tumbled by hand for one hour. The composite sample was immediately subdivided into two clean gallon bottles, capped with Teflon-lined screw-caps and stored at 4°C.

Preparation of Spiking Solutions and 100 Percent Calibration standards

Individual stock solutions of each of the five selected compounds were prepared at 1.00 mg/mL in reagent methanol. Dilutions were made using methanol to achieve the concentration levels used for spiking each 100-mL matrix sample and for preparing the 100 percent calibration standards. For each analyte under evaluation, two replicates of the unspiked reagent water were extracted using the modified Method 3560 procedure and both methanol and hexane eluent were collected to provide a proper matrix for preparation of the high and low level 100 percent recovery standards. An aliquot of the diluted spiking solution equal to that used for spiking the matrix samples was placed into these eluents to provide the required calibration standards.

Preparation of Spiked Samples

The spiking experiments were conducted for the five selected compounds--first in reagent water matrix and then in the composite ground-water matrix.

Spiking of Reagent Water--

Each compound to be evaluated was spiked at two levels. The low level spikes were prepared at a concentration which yielded a UV absorbance of what was thought to approach the Method 8610 detection limit. The high level spikes were prepared with a 5-fold higher concentration. Six replicates of the unspiked reagent water sample were also extracted using revised Method 3560. One replicate was used for the reference cell for UV determination, and two replicates were used for the preparation of the 100 percent calibration standards for the low and high spike levels. The remaining three unspiked replicates were used for the triplicate down-gradient versus up-gradient baseline determination. Thus, a sample batch consisted of 12 samples.

For each selected compound, triplicate 100-mL aliquots of reagent water were measured into a bottle with a Teflon-lined screw-cap using a graduated cylinder. The sample was then spiked with 50 µL of the appropriate spiking solution, capped, and shaken. The spiking levels of each compound in 100-mL reagent water are presented in Table 3 for low levels and Table 4 for high levels. Each spiked sample was extracted and eluted with methanol and hexane using the modified Method 3560 procedure.

Spiking of Composite Ground Water--

The composite ground-water sample was thoroughly agitated and mixed to achieve a homogeneous suspension of the sediment before each 100-mL aliquot was taken. The nonspiked, low spiked and high spiked ground-water samples were prepared as described above and in Tables 3 and 4 for spiking reagent water for 2,4-dimethylphenol, 1,2-diphenylhydrazine, 1,4-dichlorobenzene and methoxychlor. The spiking levels for 3,3'-dichlorobenzidine were reduced to 15 µg/L (50 µL of 0.03 mg/mL methanol solution) for low level spikes and 78 µg/L (50 µL of 0.16 mg/mL methanol solution) for high level spikes to obtain a more appropriate level for detection limit evaluation. In addition to the six spiked samples and six nonspiked samples, one additional nonspiked

reagent water sample was also extracted as a QC sample so that there were 13 samples per batch of spiked composite ground water.

TABLE 3. LOW SPIKE LEVELS OF SELECTED AROMATIC COMPOUNDS IN REAGENT WATER

Compound	Concentration of Spiking Solution, mg/L	Volume Spiked in 100 mL reagent water, µL	Spike Level µg/L
Polar Aromatic Compounds			
3,3'-Dichlorobenzidine	45	50	23
2,4-Dimethylphenol	300	50	150
1,2-Diphenylhydrazine	30	50	15
Nonpolar Aromatic Compounds			
1,4-Dichlorobenzene	1200	50	600
Methoxychlor	60	50	30

TABLE 4. HIGH SPIKE LEVELS OF SELECTED AROMATIC COMPOUNDS IN REAGENT WATER

Compound	Concentration of Spiking Solution, mg/L	Volume Spiked in 100 mL reagent water, µL	Spike Level µg/L
Polar Aromatic Compounds			
3,3'-Dichlorobenzidine	230	50	115
2,4-Dimethylphenol	1500	50	750
1,2-Diphenylhydrazine	150	50	75
Nonpolar Aromatic Compounds			
1,4-Dichlorobenzene	6000	50	3000
Methoxychlor	300	50	150

UV Analysis of Spiked Samples and 100 Percent Calibration Standards

The UV spectrophotometric conditions described above for matrix background evaluation were used for analyzing the 100 percent calibration standards and the spiked sample eluents. For each analyte set under evaluation, three baseline UV spectra were first determined by scanning each of the three replicates of the unspiked sample versus the replicate of the unspiked sample reserved as the reference. Then, the three low spike replicate extracts were recorded on the corresponding nonspike repliate chart followed by the three high spike replicates, similarly. Thus, the UV spectral chart for a given replicate set consisted of the baseline (unspiked), the low spike, and the high spike spectra overlaid as a group so that absorbance could be easily compared at any specific wavelength.

Sample cells were not rinsed between replicates of the same analyte at the same spiking level or when changing from a lower spiking level to a higher level. They were shaken upside down while empty to remove all liquid from the previous sample. Using this method, carry-over residue was estimated at 10-20 µL which represents approximately 5 parts per thousand.

When changing from hexane to methanol eluates or vice versa, or when changing from one analyte set to a second analyte set, the cells were thoroughly rinsed with reagent solvent of the next type to be used and drained thoroughly, then dried in air.

SECTION 5

RESULTS AND DISCUSSION

EVALUATION OF MATRIX EFFECTS OF UNSPIKED GROUND-WATER SAMPLES

Instrument Background Evaluation

The spectra for air versus air and solvent versus solvent are shown in Figure 1. No appreciable difference was observed between these spectra. They all indicate a short-term noise level of about 0.001 a.u. and a baseline non-linearity of about $\pm$ 0.002 a.u. which is normal for the Cary 17 spectrophotometer in the 220-400 nm range.

Evaluation of the Cartridge Cleanup and Solvent Elution Procedure

UV absorption due to residual interstitial solvent carried out with a subsequent elution solvent was of no concern since, (1) the UV cutoff wavelength for reagent methanol is 203 nm and that for reagent hexane is 186 nm and (2) by applying vacuum after each solvent elution, most of the residual solvent would have been eliminated from the cartridge before the next solvent elution.

The precision of the Method 3560 cleanup procedure was evaluated by the reproducibility of the UV spectra for reagent water procedure blanks. Typical results are shown in Figure 2 for both methanol and hexane eluents. In all, 15 reagent water blanks were examined in the reagent water spiking experiments and another 5 were examined with the ground water matrix effects study. Only one of these samples produced a spectrum different from those shown in Figure 2. These spectra indicate that 230-400 nm is an appropriate range for Method 8610 UV absorbance determination when used in conjuction with Method 3560. The variation of UV absorbance within the 230-400 nm range for both methanol and hexane eluates is estimated to be 0.005 absorption units.

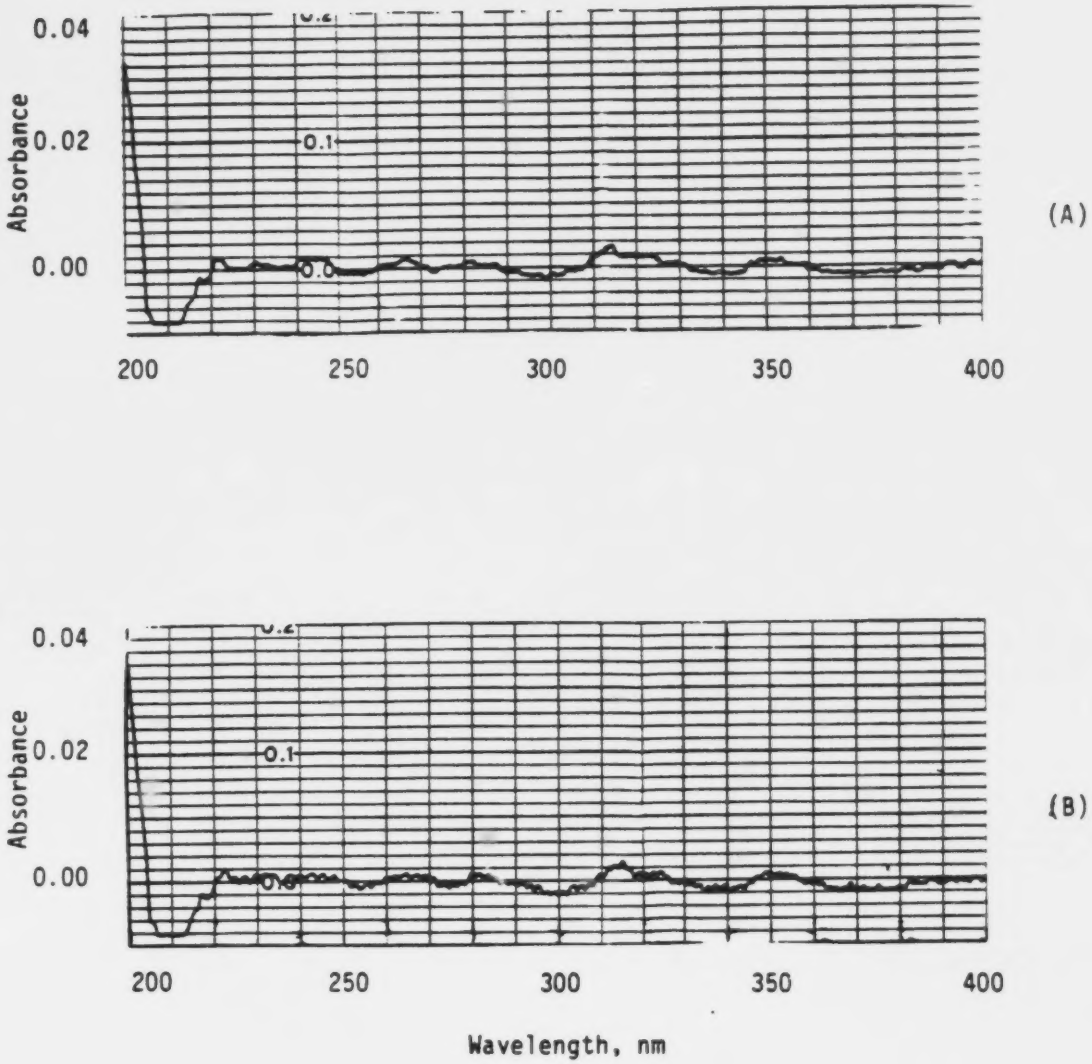


Figure 1. Instrument noise levels of the Cary 17 spectrophotometer (A) air versus air, (B) methanol versus methanol

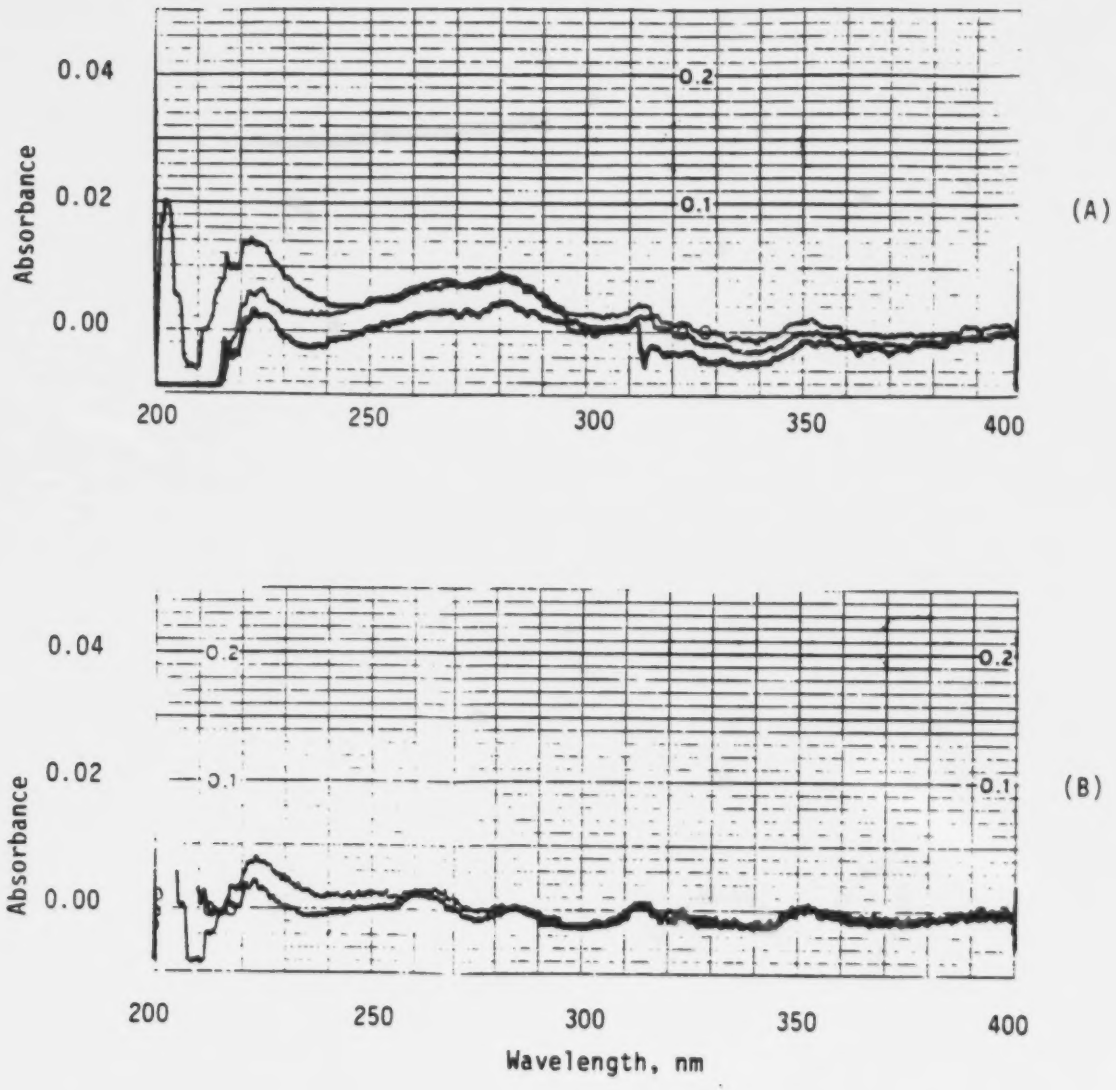


Figure 2. Reproducibility of the UV spectra of replicates from a Method 3560 procedure blank (A) methanol eluents, (B) hexane eluents.

Matrix Effects for Unspiked Ground-Water Samples

The background for the ground-water samples tested was investigated in two ways. First, the differences in the UV spectra of the sample eluate and procedure blank were obtained to show the amount of UV absorbing material in the sample. These are presented as spectra (a) in Figures 3 through 6. Second, a differential mode UV scan was obtained using the solvent eluant of field sample replicate 1, versus replicate 2, to simulate a noncontaminated situation for down-gradient versus up-gradient testing. These are shown as spectra (b) in Figures 3 through 6. Results of the UV analysis of unspiked samples indicate that three of the seven samples under evaluation have low UV background (0.03 a.u. at 230 nm). They are Samples A, B, and C as shown in Figure 3. Three samples have a slightly higher UV background (0.04-0.06 a.u. at 230 nm). These are Samples D, E, and F as presented in Figure 4. Only Sample G has an unusually high UV background (0.25 a.u. at 230 nm) as presented in Figure 5. It appears that methanol elution was able to elute most of the UV active substances in all the samples. The subsequent hexane eluents did not show appreciable absorbance. The UV spectra of hexane eluents of Samples F and G are presented in Figure 6.

For the seven ground waters, the "single replicate" down-gradient versus up-gradient absorbance differences averaged 0.012 $\pm$ .005 a.u. at 230 nm, 0.009 $\pm$ .005 a.u. at 250 nm, and 0.008 $\pm$ .004 a.u. at 280 nm; thus, the absorbance difference required to conclude that a given down-gradient water sample contains higher levels of UV absorbing material than a corresponding up-gradient sample varies with the wavelength used. For wavelengths between 230 and 300 nm, about 0.02 a.u. difference is required, while about 0.01 a.u. difference would be required between 300 and 400 nm.

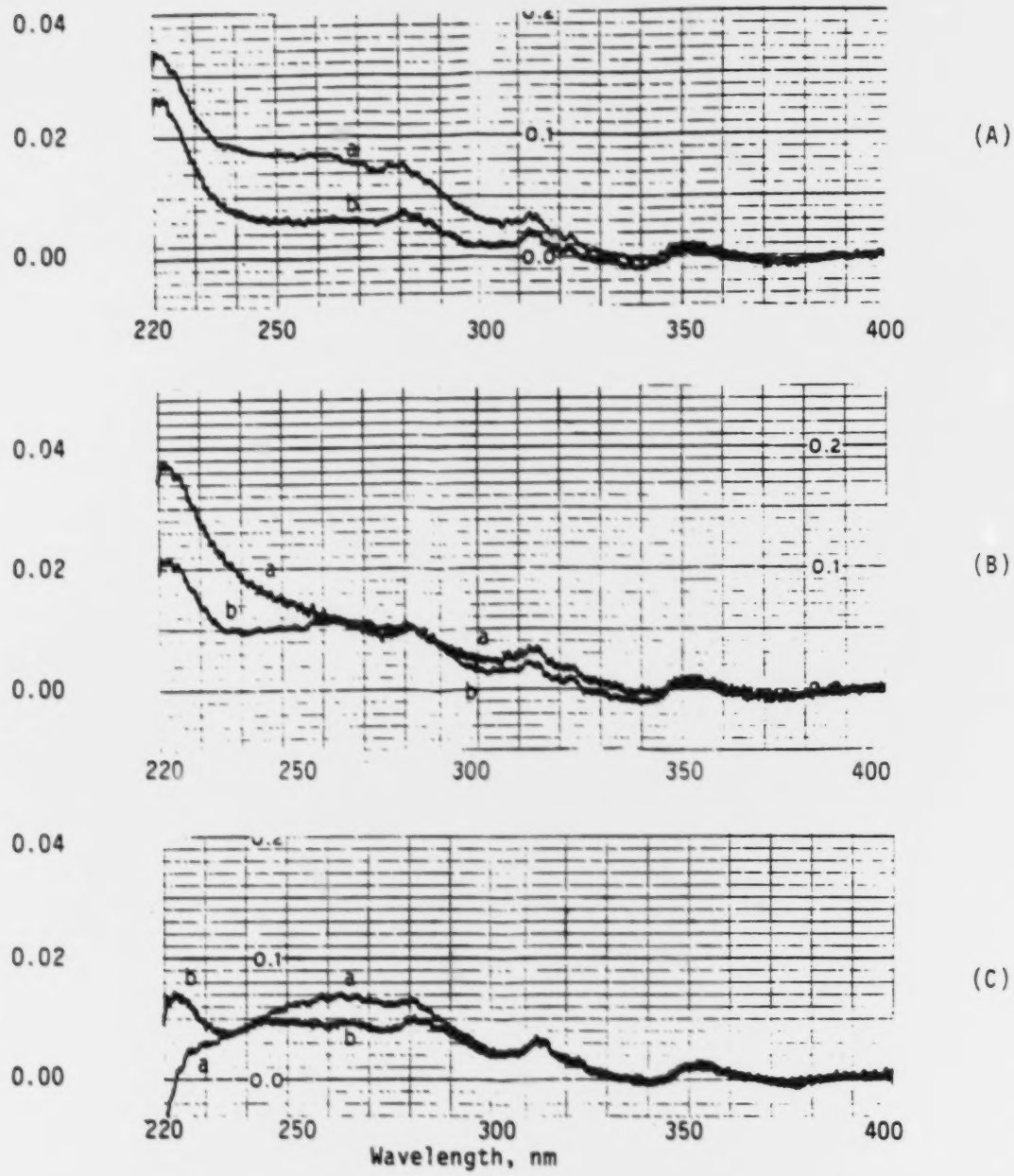


Figure 3. UV spectra of methanol eluents from low background ground-water samples (A) sample A (B) sample B (C) sample C obtained with reference (a) procedure blank (b) methanol eluent of duplicate sample.

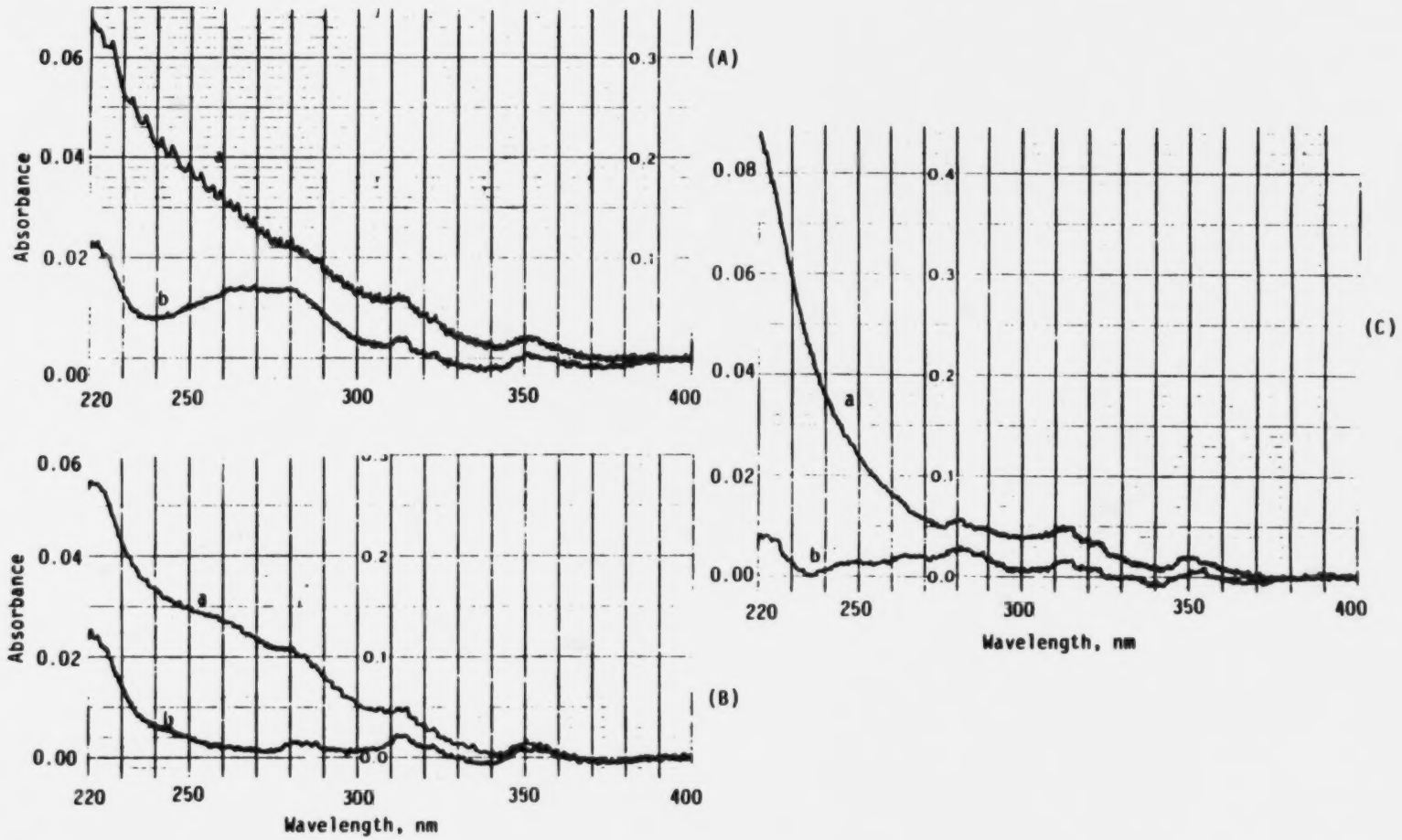


Figure 4. UV spectra of methanol eluents from medium background ground-water samples (A) sample D (B) sample E (C) sample F obtained with reference (a) procedure blank (b) methanol eluent of duplicate sample.

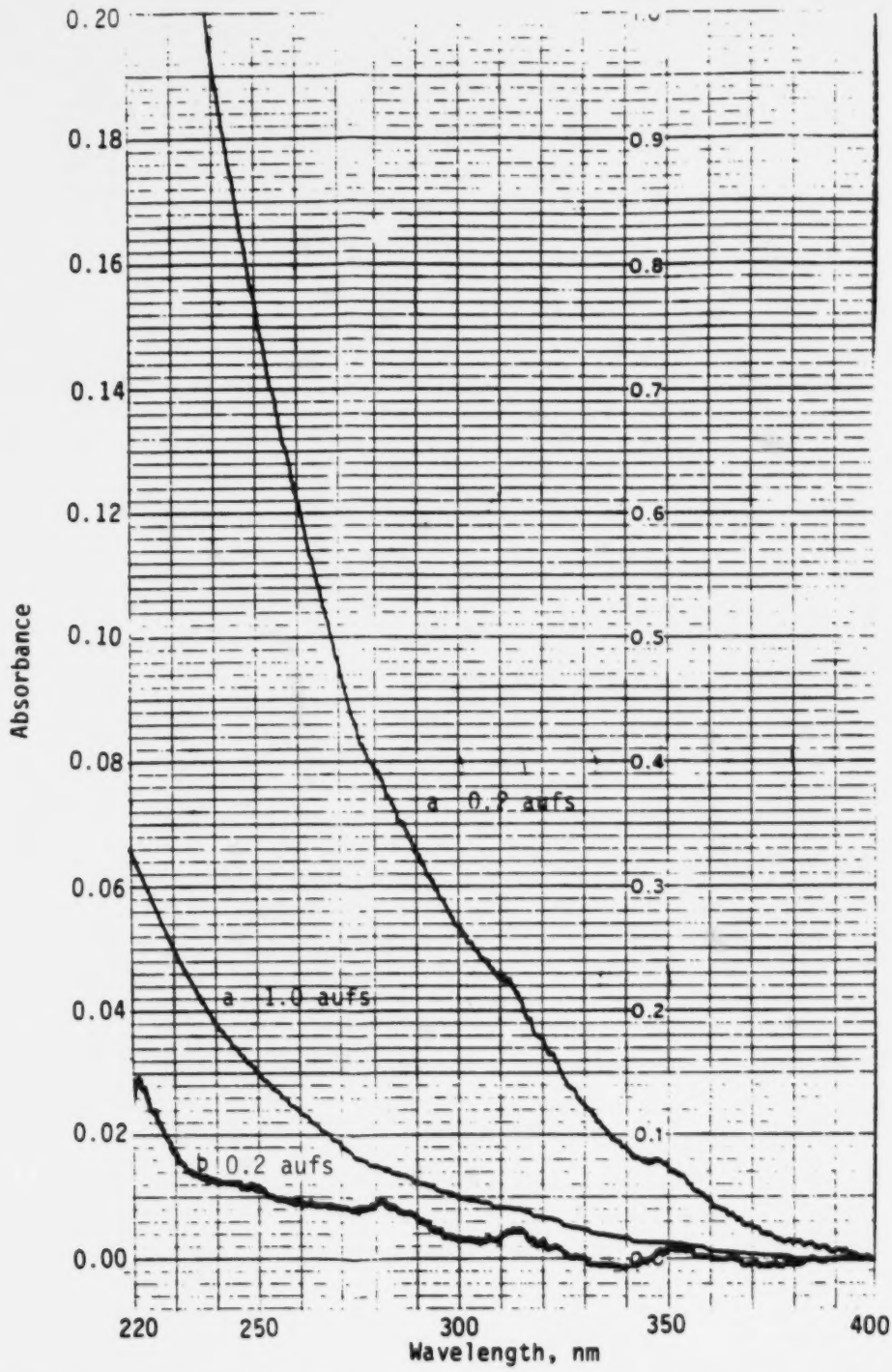


Figure 5. UV spectra of methanol eluents from high background groundwater sample (sample G) obtained with reference (a) procedure blank (b) methanol eluent of duplicate sample.

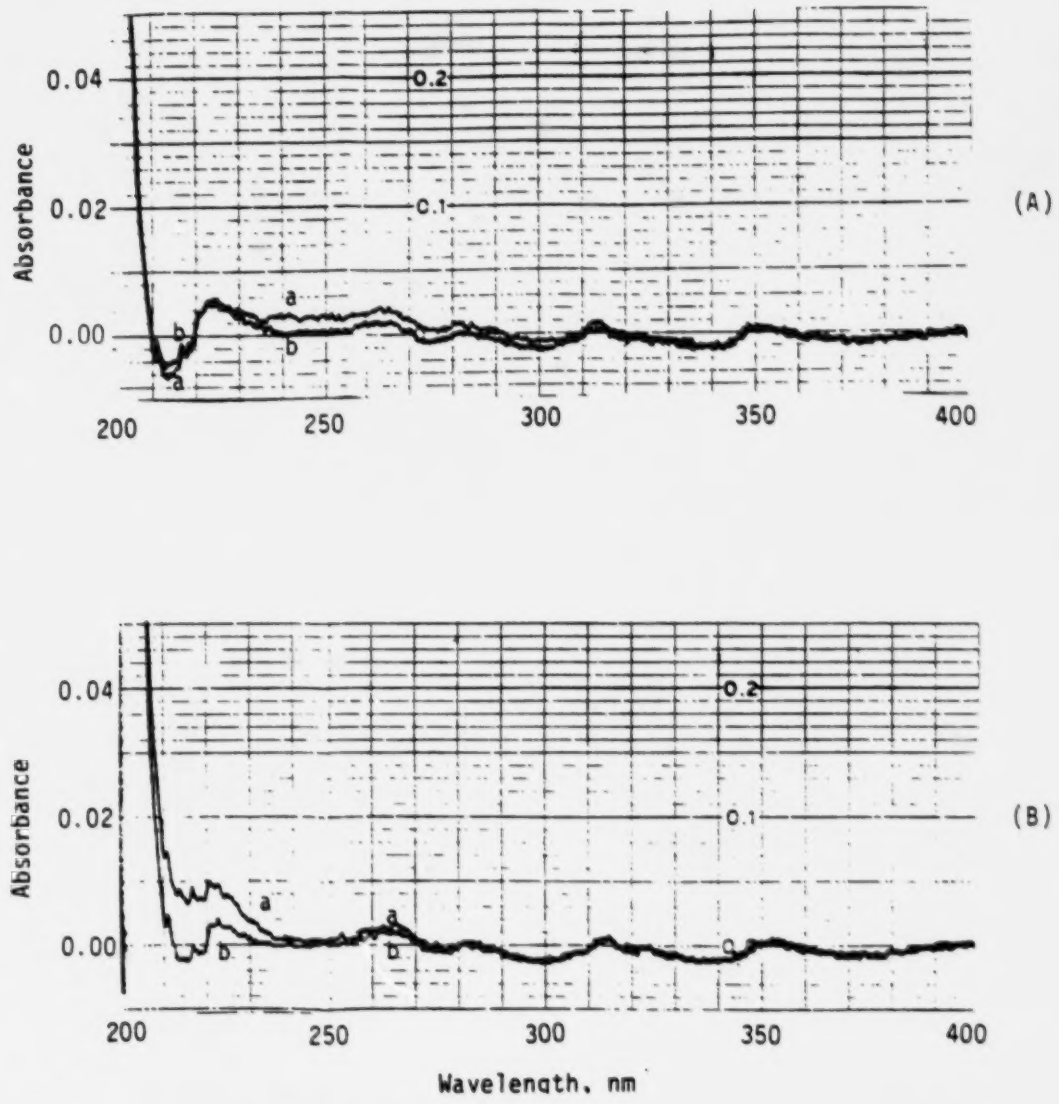


Figure 6. UV spectra of hexane eluents from high and medium background ground water (A) sample F (B) sample G obtained with reference (a) procedure blank (b) hexane eluent of duplicate sample.

EVALUATION OF SPIKE RECOVERIES OF REAGENT WATER

The results of triplicate analyses of the low and high level spiked reagent water samples are presented in Tables 5 and 6, respectively. One representative replicate of the UV spectra for each of the five selected compounds is presented in Figures 7-11. For the low level spikes (Table 5), the overall recoveries for all five compounds are higher than 85 percent with the averages for three replicates ranging from 86 to 108 percent. The percent RSD for all compounds are within 5 percent except for methoxychlor which has a percent RSD of 16. For the high spiking level (Table 6), the overall average recovery for all five analytes ranged from 79 to 102 percent. The percent RSD values for four analytes are within 5 percent, while the fifth, methoxychlor has a percent RSD of 16 percent (low level) and 17 percent (high level). Tables 5 and 6 also show that the polar compounds are almost completely eluted from the cartridges with methanol, but the two nonpolar compounds were eluted partially in both methanol and hexane.

Although the recoveries of 1,2-diphenylhydrazine were calculated, this compound is unstable in water and in methanol. The UV spectrum determined for 1,2-diphenylhydrazine in reagent water after storage at room temperature for 48 hours is shown in Figure 12, and the UV spectrum acquired immediately after the solution was prepared is shown in Figure 13. Comparison of these two figures shows both λ_{max} and extinction coefficient shifts. The increased absorbance at 312 nm is probably due to rearrangement to benzidine or oxidation to azobenzene. 1,2-Diphenylhydrazine is typical of some of the Method 8610 analytes for which stability in water and elution solvents needs to be further investigated. For example, benzotrichloride is also known to rapidly decompose in water.

EVALUATION OF SPIKE RECOVERIES OF COMPOSITE GROUND WATER

The excellent spike recoveries and precisions observed for the reagent water experiments, described above, were not duplicated for the composite ground-water spiking experiments. The spike recoveries obtained by working

TABLE 5. RECOVERY OF MODIFIED METHOD 3560 OF SELECTED METHOD 8610 PARAMETERS SPIKED INTO REAGENT WATER AT LOW LEVEL

Compound	Amount Spiked, µg/L	Percent Recovery Given Elution Solvent						Total Percent Recovery			Average	SD[a]	RSD,[b] %
		Methanol Eluent			Hexane Eluent								
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3			
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	23	88	85	85	0	0	0	88	85	85	86	1.7	2
2,4-Dimethylphenol	150	94	94	100	3	3	0	97	97	100	98	1.7	2
1,2-Diphenylhydrazine[c]	15	100	100	100	10	10	0	110	110	100	106	5.8	5
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	600	71	79	86	19	14	10	90	93	96	93	3.0	3
Methoxychlor	30	64	72	55	64	28	42	128	100	97	108	17	16

[a]SD = Standard Deviation.

[b]RSD,% = Percent Relative Standard Deviation.

[c]This compound is not stable in water, recovered amounts included the degradation products.

TABLE 6. RECOVERY OF MODIFIED METHOD 3560 OF SELECTED METHOD 8610 PARAMETERS SPIKED INTO REAGENT WATER AT HIGH LEVEL

Compound	Amount Spiked, µg/L	Percent Recovery Given Elution Solvent						Total Percent Recovery			Average	SD[a]	RSD,[b] %
		Methanol Eluent			Hexane Eluent								
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3			
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	116	95	88	95	0	0	0	95	88	95	93	4.0	4
2,4-Dimethylphenol	750	93	89	87	2	3	4	95	92	91	93	2.1	2
1,2-Diphenylhydrazine[c]	75	98	87	98	5	10	9	103	97	107	102	5.0	5
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	3000	68	67	70	10	12	10	78	79	80	79	1.0	1
Methoxychlor	150	53	55	51	13	39	33	66	94	84	81	14	17

[a] SD = Standard Deviation.

[b] RSD,% = Percent Relative Standard Deviation.

[c] This compound is not stable in water, recovered amounts included the degradation products.

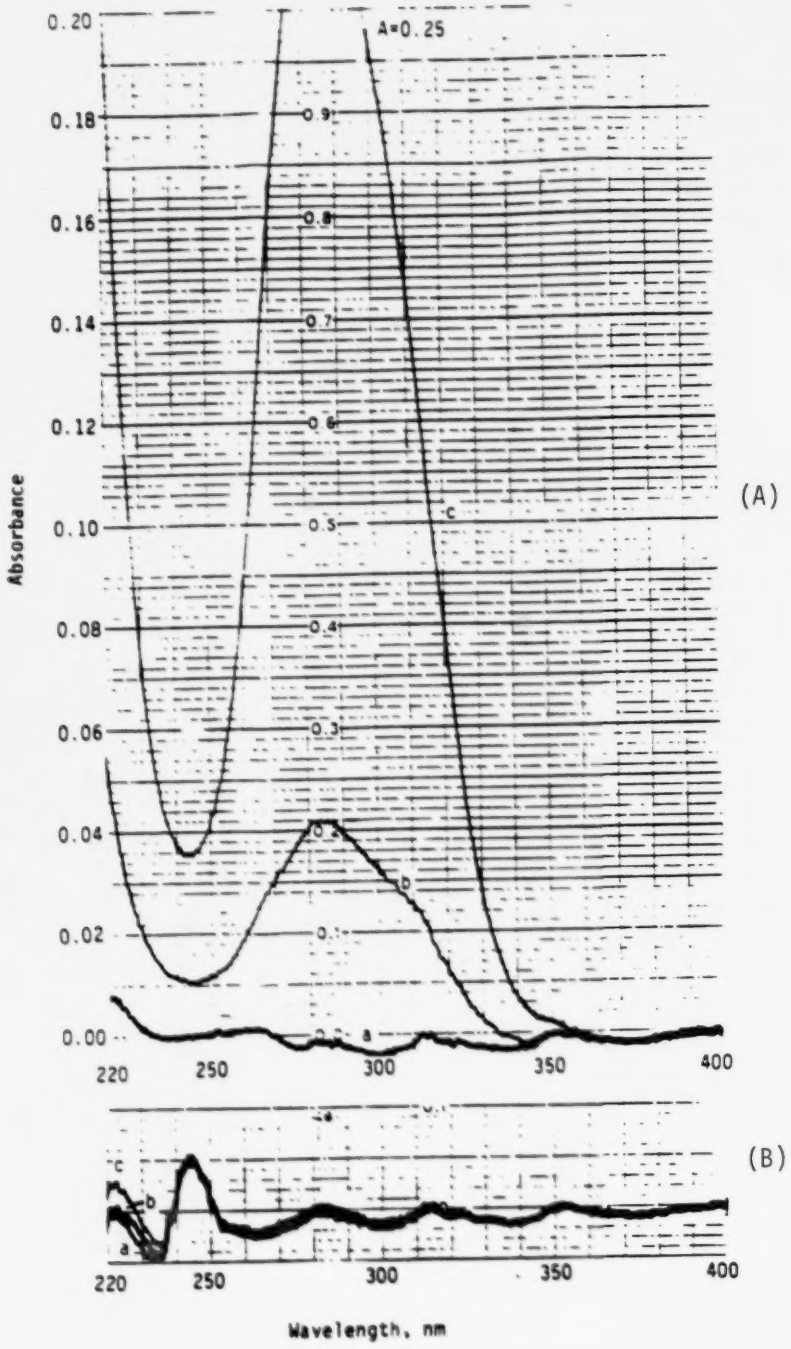


Figure 7. UV spectra of methanol and hexane eluents from 3,3'-dichlorobenzidine spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 23 µg/L (c) 116 µg/L.

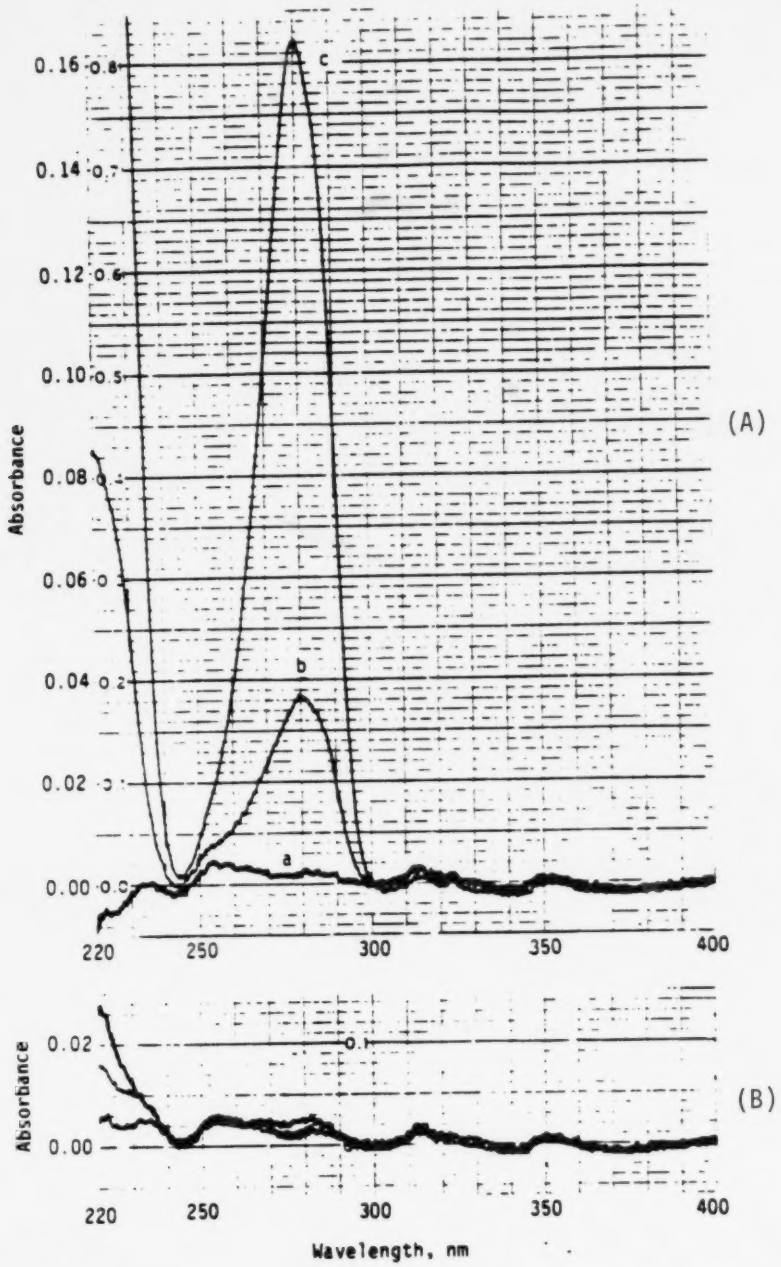


Figure 8. UV spectra of methanol and hexane eluents from 2,4-dimethylphenol spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L.

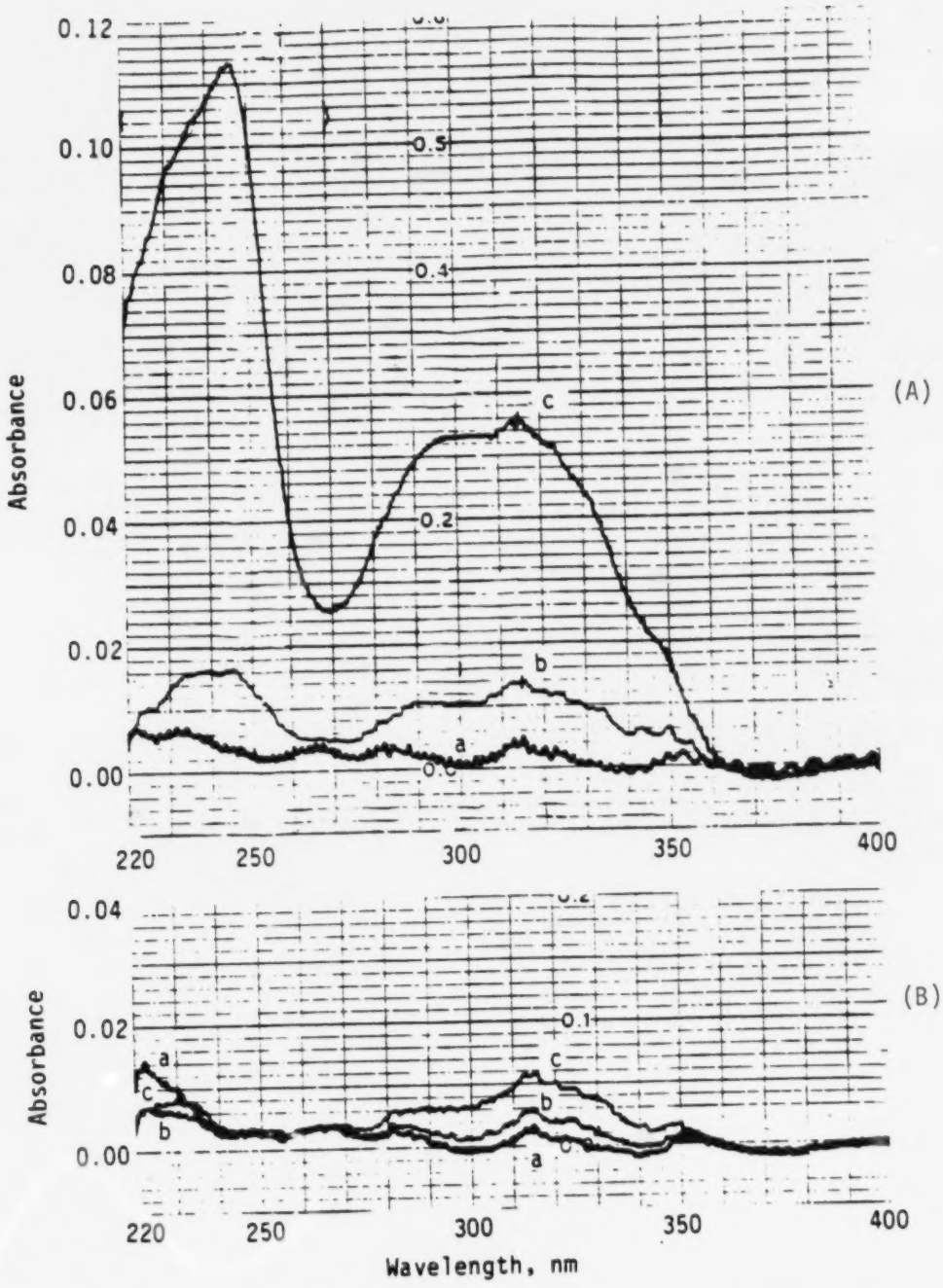


Figure 9. UV spectra of methanol and hexane eluents from 1,2-diphenylhydrazine spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L.

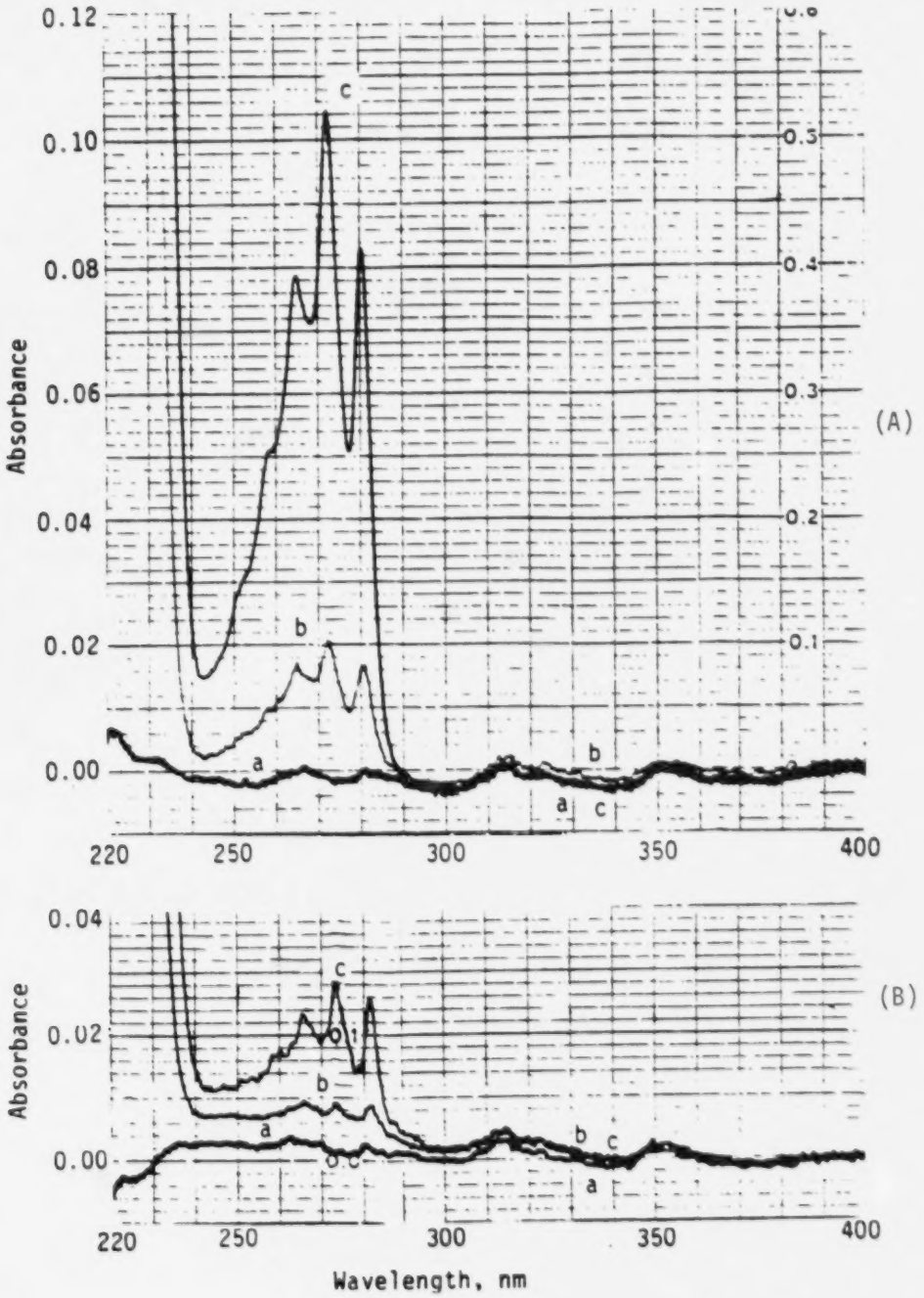


Figure 10. UV spectra of methanol and hexane eluents from 1,4-dichlorobenzene spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L.

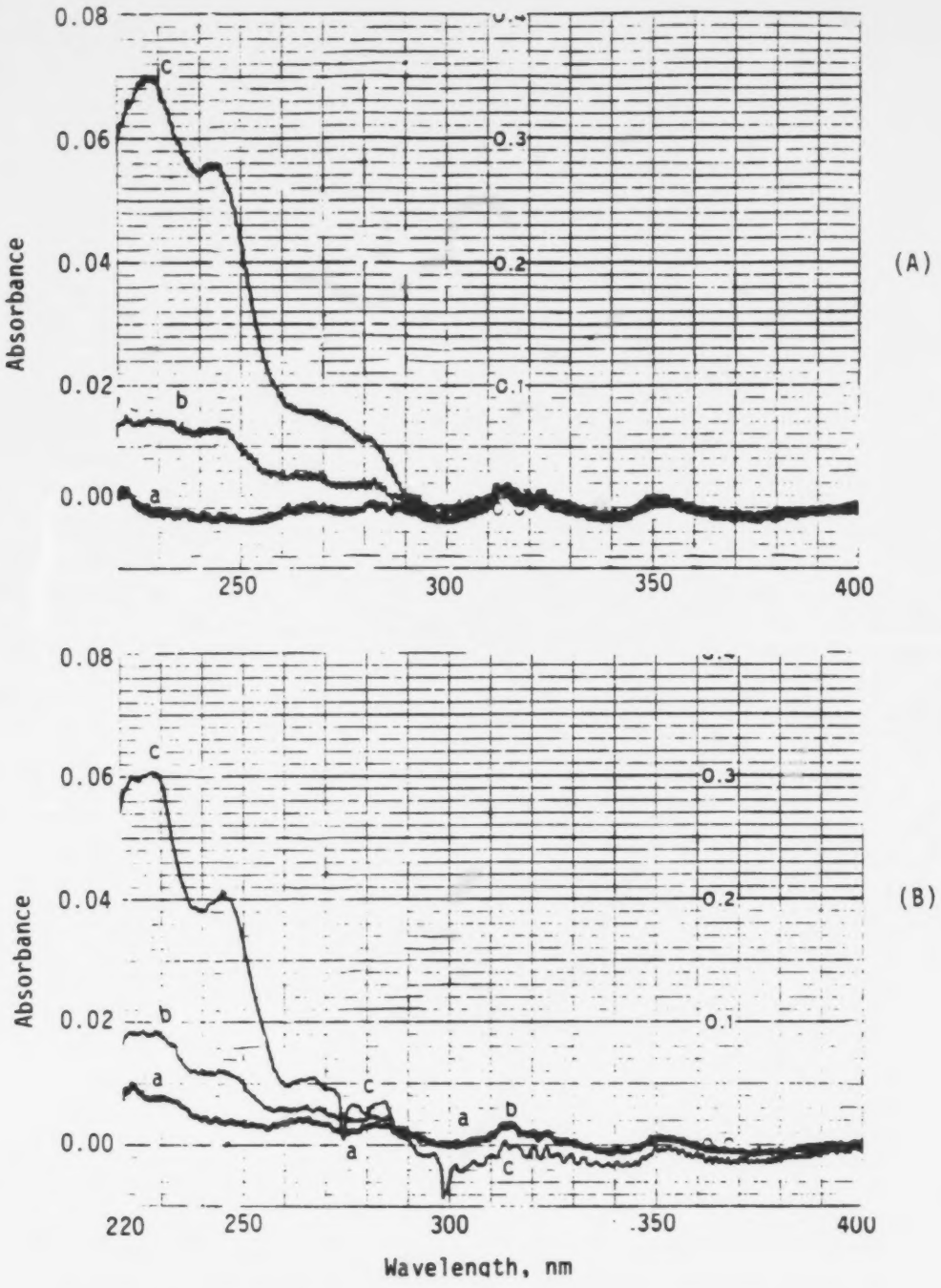


Figure 11. UV spectra of methanol and hexane eluents from methoxychlor spiked reagent water (A) methanol eluents (B) hexane eluents: Spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L.

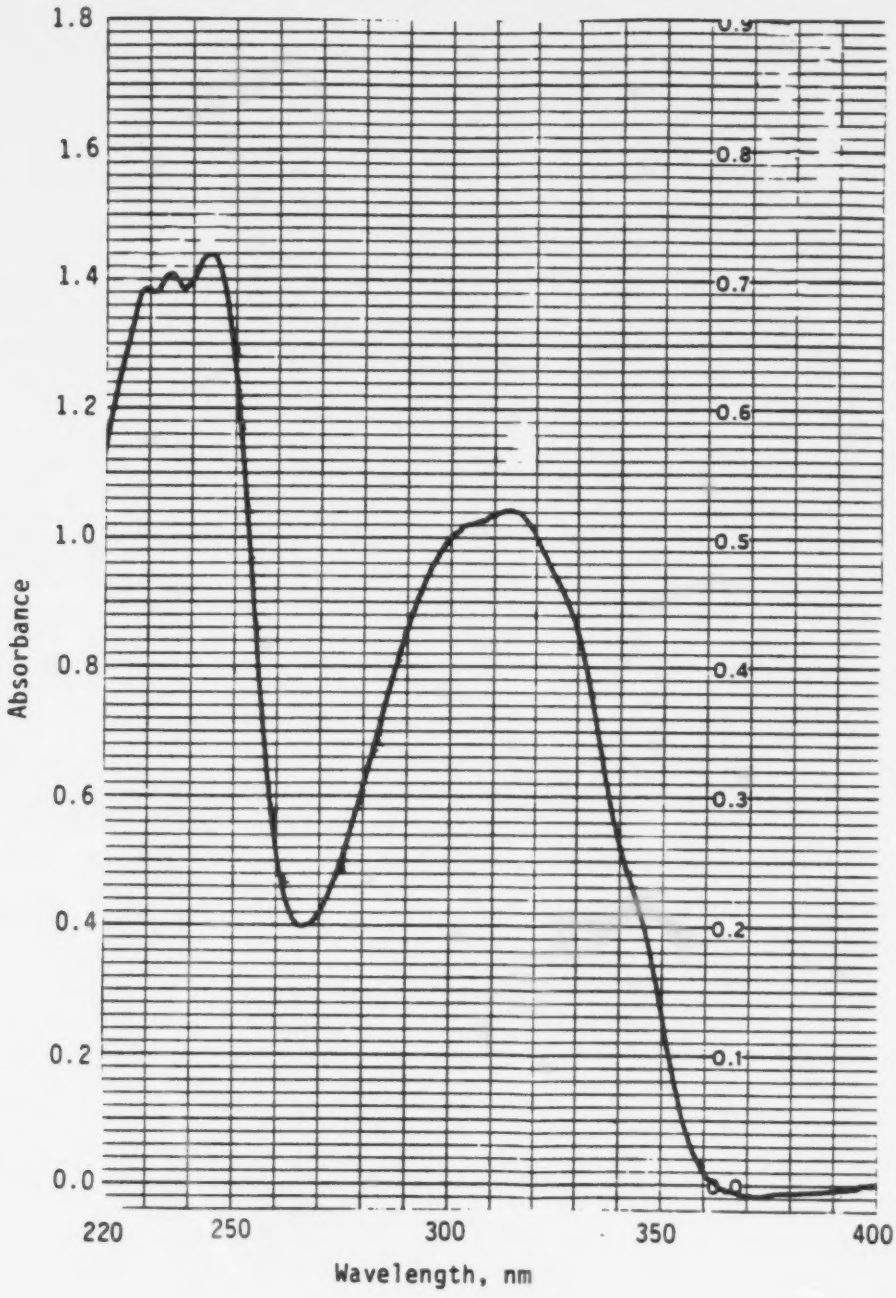


Figure 12. UV spectrum of 1,2-diphenylhydrazine at a concentration of 20 mg/L in reagent water after storage at room temperature for 48 hours (reagent water reference).

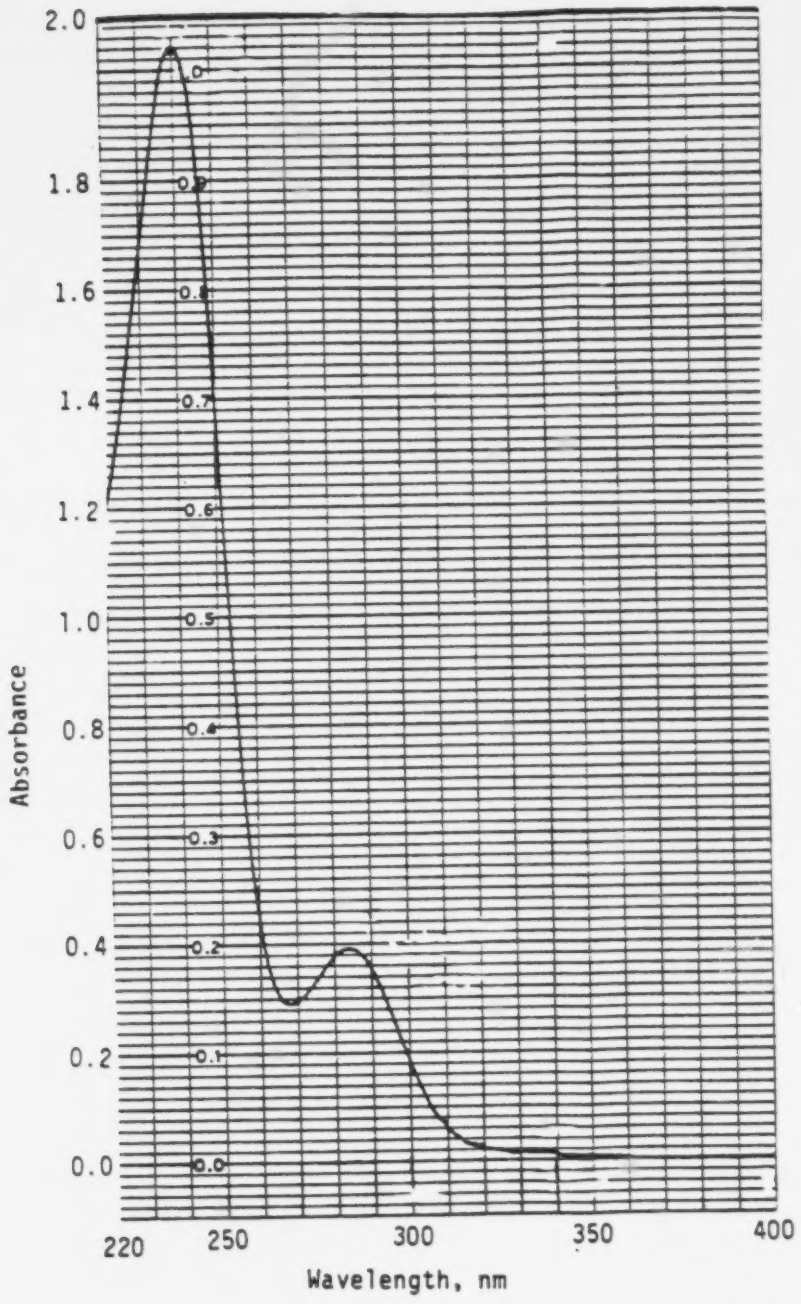


Figure 13. UV spectrum of 1,2-diphenylhydrazine at a concentration of 20 mg/L in reagent water (reagent water reference).

up the spectral data for the composite water in the same fashion as for the reagent water are shown in Table 7 for the low spiking level and in Table 8 for the high spiking level. In generating the recovery results for Tables 7 and 8, absorbance was determined by measuring the difference at the respective λ_{max}'s between the traces for the unspiked sample versus the low and high spiked samples. The extremely poor reproducibility observed for these composite ground-water spikes is due to a variation in the recovery of background UV absorbing material in the methanol reverse phase cartridge eluate. To provide a representation of the kind of variation observed, the spectral charts for all three of the methanol eluate replicate determinations for all five of the spiked analytes are provided in Appendix A. To balance the recorder signal, the composite sample with the lowest measured absorbance was used in the reference cell. The variation in the flatness of the 15 spectra for unspiked samples in Appendix A provides a range of uncertainty in the data for the spectra of the low and high spike methanol eluates. The spectra obtained for the hexane eluates of the composite ground-water samples are not included here since they were equivalent in all quality respects to those for the reagent water samples (see, for example, Figures 6 through 11).

Since the spectral variations of unspiked samples all had similar wavelength/intensity profiles, it was felt that a baseline correction could be applied to the Appendix A spectra for the spiked samples to give a more correct representation of the actual spike recoveries obtained. Thus, pseudo-baselines as shown in the Appendix A spectra were used to correct the data for this problem, and the spike recoveries obtained are shown in Table 9 (low spiking level) and Table 10 (high spiking level). While the methanol eluate recoveries shown in Tables 9 and 10 for the composite ground water compare favorably with those of Tables 5 and 6 for the reagent water, the use of pseudo-baselines prevents any detailed comparisons between these methanol data sets. The hexane eluates, however, do show some significant differences in recoveries for methoxychlor with averages of 44 and 28 percent recovered in the low and high spike samples, respectively, for reagent water compared to 5 and 6 percent recovered in the low and high spike samples for composite ground water. In contrast, there was no hexane eluate recovery difference

TABLE 7. RECOVERY OF MODIFIED METHOD 3560 OF SELECTED METHOD 8610 PARAMETERS SPIKED INTO COMPOSITE GROUND WATER AT LOW LEVEL WITHOUT BASELINE CORRECTION

Compound	Amount Spiked, µg/L	Percent Recovery Given Elution Solvent						Total Percent Recovery			Average	SD[a]	RSD,[b] %
		Methanol Eluent			Hexane Eluent								
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3			
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	15	81	11[c]	58	0	0	0	81	11	58	32	42	132
2,4-Dimethylphenol	150	174[c]	184[c]	55[c]	0	0	0	174	184	55	138	72	52
1,2-Diphenylhydrazine[d]	15	178[c]	114[c]	128[c]	25	25	37	203	139	165	169	32	19
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	600	-21[c]	-24[c]	-33[c]	14	14	14	-7	-10	-19	-12	6.2	-52
Methoxychlor	30	-92[c]	+36[c]	-156[c]	7	0	7	-85	+36	-149	-66	94	142

[a] SD = Standard Deviation.

[b] RSD,% = Percent Relative Standard Deviation.

[c] Possible matrix particulate interference.

[d] This compound is not stable in water, recovered amounts include the degradation products.

TABLE 8. RECOVERY OF MODIFIED METHOD 3560 OF SELECTED METHOD 8610 PARAMETERS SPIKED INTO COMPOSITE GROUND WATER AT HIGH LEVEL WITHOUT BASELINE CORRECTION

Compound	Amount Spiked, µg/L	Percent Recovery Given Elution Solvent						Total Percent Recovery			Average	SD[a]	RSD,[b] %
		Methanol Eluent			Hexane Eluent								
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3			
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	75	87	61[c]	85	0	0	0	87	61	85	78	14	18
2,4-Dimethylphenol	750	115[c]	91[c]	121[c]	0	2	0	115	93	121	110	15	13
1,2-Diphenylhydrazine[d]	75	78	81	88	19	21	19	97	102	107	102	5	5
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	3000	42[c]	46[c]	36[c]	14	12	13	56	58	49	54	5	9
Methoxychlor	150	18[c]	28[c]	16[c]	6	7	4	24	35	20	26	8	30

[a]SD = Standard Deviation.

[b]RSD,% = percent Relative Standard Deviation.

[c]Possible matrix particulate interference.

[d]This compound is not stable in water, recovered amounts included the degradation products.

TABLE 9. RECOVERY OF MODIFIED METHOD 3560 OF SELECTED METHOD 8610 PARAMETERS SPIKED INTO COMPOSITE GROUND WATER AT LOW LEVEL QUANTIFIED USING PSEUDO BASELINE AS NECESSARY

Compound	Amount Spiked, µg/L	Percent Recovery Given Elution Solvent						Total Percent Recovery			Average	SD[a]	RSD,[b] %
		Methanol Eluent			Hexane Eluent								
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3			
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	15	81	62[c]	58	0	0	0	81	62	5	67	12	18
2,4-Dimethylphenol	150	110[c]	105[c]	115[c]	0	0	0	110	105	115	110	5	5
1,2-Diphenylhydrazine[d]	15	--	143[c]	171[c]	25	25	37	--	168	208	188	--	--
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	600	86[c]	86[c]	71[c]	14	14	14	100	100	85	95	9	9
Methoxychlor	30	36[c]	36[c]	32[c]	7	0	7	43	36	39	39	4	10

[a]SD = Standard Deviation.

[b]RSD,% = Percent Relative Standard Deviation.

[c]Possible matrix particulate interference. Pseudo baseline was used for quantification.

[d]This compound is not stable in water, recovered amounts include the degradation products.

TABLE 10. RECOVERY OF MODIFIED METHOD 3560 OF SELECTED METHOD 8610 PARAMETERS SPIKED INTO COMPOSITE GROUND WATER AT HIGH LEVEL QUANTIFIED USING PSEUDO BASELINE AS NECESSARY

Compound	Amount Spiked, µg/L	Percent Recovery Given Elution Solvent						Total Percent Recovery			Average	SD[a]	RSD,[b] %
		Methanol Eluent			Hexane Eluent								
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3			
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	75	87	74[c]	85	0	0	0	87	74	85	82	7	8
2,4-Dimethylphenol	750	115[c]	91[c]	121[c]	0	2	0	115	93	121	110	15	13
1,2-Diphenylhydrazine[d]	75	74	74	74	19	21	19	93	95	93	94	1	1
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	3000	72[c]	80[c]	70[c]	14	12	13	86	92	83	87	4	5
Methoxychlor	150	52[c]	47[c]	47[c]	6	7	4	58	54	51	54	4	6

[a] SD = Standard Deviation.

[b] RSD,% = Percent Relative Standard Deviation.

[c] Possible matrix particulate interference. Pseudo baseline was used for quantification.

[d] This compound is not stable in water, recovered amounts included the degradation products.

between reagent water and ground water for the other nonpolar analyte, 1,4-dichlorobenzene which averaged between 11 and 14 percent for all four data sets.

While the actual chemical mechanism causing the wide variability in recovery of UV absorbing material from composite ground-water samples cannot be identified from the data presently available, the cause of the variability can definitely be attributed to the ground water itself rather than laboratory procedural variations. The reasons are:

- The same lot of reverse phase cartridges, elution solvents and spiking media were used for all experiments.
- All extracts were produced by the same laboratory technician using the same apparatus and identical laboratory procedures in the same laboratory location.
- Sets of extracts were generated sequentially with no time delay between the reagent water set and the ground-water set.

Finely divided particulate material in the composite ground water is most likely the cause of variation in UV absorbance recovery. Two of the ground-water samples used to make the composite sample had high levels of particulate material which, after compositing, lost its previous tendency to settle. While the particulate material in the individual samples would completely settle overnight, about 90 percent of the suspended material in the composite sample remained in suspension after overnight standing. To ensure homogeneity, both composited and non-composited ground water was well-shaken before 100-mL aliquots were taken for extraction. Therefore, all composite ground-water replicates provided about the same amount of suspended particulate to the reverse phase extraction cartridges. Although the extraction cartridges are equipped with a 20 µm polyethylene frit at the top, the suspended particulate matter was not completely removed as some of the particulate matter color was visible on the column bed. For the composite ground water, the methanol elution removed some of this particulate matter from the cartridge while none was recovered in methanol eluates of the non-composited ground waters. The recovery of particulate matter into the methanol eluate occurred for every unspiked and spiked composite ground-water

sample and the amount varied over a range of a factor of three with the total amount present averaging about 0.5 mg. Less than one percent of the suspended particulate matter in the 100-mL aqueous sample was recovered in the methanol fractions.

While it seems clear that suspended particulate matter somehow produces the variability in UV absorbance recovery observed, the mechanism by which this variation is caused cannot be determined by the data available. Some possible mechanisms might include the following:

- Suspended particles in the UV beam of the spectrophotometer might have caused light scattering. However, the particulate matter in the methanol eluents were apparently settled before UV spectra acquisition and an effort was made to avoid any agitation which might result in transfer of settled particles with the aliquot for UV analysis.

- Organic or inorganic UV absorbing material adsorbed on the particulate matter may be only slowly extractable with methanol, and, therefore, is generated after elution only by methanol leaching of the variable amount of particulate matter found in the methanol eluate. However, the UV recovery deviation does not appear to quantitatively correlate with the amount of recovered particulate matter.

- Inorganic material which has UV absorption might be leached from the particulate matter on the extraction cartridge by the methanol eluate, and the variability might be produced by flow channelling variations in this elution step.

While quantitative conclusions are not possible from the composite ground-water data, the results do suggest that removing particulate matter before extraction might provide recovery results approaching those obtained for reagent water. Further experimentation on the composite ground water used was not possible since it was consumed in the spiking experiments. However, it was possible to further examine the composite ground-water extract methanol eluates for evidence of the possible mechanisms by which the inorganic particulate matter could have caused the matrix recovery variability. Centrifugation and filtration (0.5 micron) of the three nonspiked methanol eluates with the highest matrix background recovery were tested to determine if suspended particulate matter could be the cause of the

variability observed. Composited reagent water blank extract methanol eluates were used as the reference sample. Each of the three composite water methanol eluates was examined against the composite reference three times: (1) after settling for about 1 hour, (2) after centrifugation at 2300 rpm for 10 minutes, and (3) after filtration (0.5 micron). Centrifugation and filtration had no effect on the UV trace for any of the three non-spike composite ground-water methanol eluates. Therefore, particulate matter in the UV measurement beam was not the cause of the recovery variability. To determine if the variability was caused by dissolved carbonate anion, these same methanol eluates were acidified with HCl and then purged with nitrogen to remove CO_2. However, all three samples became yellow and more UV-opaque. This experiment provided no information.

Analysis of composite ground-water methanol eluates for dissolved cations and anions as the cause of the UV recovery variability was also tested. For this purpose, two sets of six spiked ground-water methanol eluates were selected--one set for cation analysis and the other set for anion analysis. Each set consisted of three samples with the highest observed matrix UV recovery and three samples with the lowest matrix UV recovery. Reference UV spectra of all 12 samples were obtained against the composite reagent water methanol eluate (see above). ICAP analysis for 24 metals showed no differences among the six replicates, and only Ca and Fe were present above the detection limit. Likewise, for the anions, there were no correlations between the levels of chloride, sulfate and nitrate and the amount of matrix UV absorbance recovery. Thus, the variability of the matrix UV recovery which could be associated with the particulate matter in the composited ground water cannot presently be demonstrated.

EVALUATION OF METHOD 8610 SENSITIVITY

Because of the matrix UV recovery variability observed for the composited ground water, only the reagent water results are useful for predicting Method Detection Limits in the 230 to 400 nm range. As shown in spectra (a) of Figures 7-11, an absorbance reading of 0.02 units is readily discernable from the background absorbance of reagent water. Using an

absorbance reading of 0.02 absorbance units as a decision level for a positive response is four times higher than the proposed Method 8610 decision limit of 0.005 absorbance units. The theoretical detection limits for Method 8610 analytes can be calculated using the Beer-Bouguer Law and 0.02 absorbance units decision limit as well as by making several assumptions with respect to the method and compounds under consideration. These assumptions include (1) the use of a 100-mL sample size, (2) an eluent volume of 5.0 mL of methanol or hexane, (3) analyte was 100 percent recovered, and, (4) analysis without further concentration. The EDLs for Method 8610 analytes are presented in Appendix B in Table B-1 for polar analytes and in Table B-2 for nonpolar analytes. Using these calculated values, only 28 percent of the 129 Method 8610 analytes are estimated to have 10 µg/L or lower detection limits and 68 percent are estimated to have 50 µg/L or lower detection limits.

SECTION 6

QUALITY ASSURANCE

Quality assurance measures in effect throughout the program included the following:

- The performance of the Cary 17 DX Spectrophotometer was evaluated daily for air versus air and solvent versus solvent, to determine the instrument background noise level and to zero the instrument baseline.

- The Cary 17 DX Spectrophotometer was calibrated for 0 and 100 percent transmittance and the wavelength and absorbance readings were verified daily with replicates of benzene calibration standards. These data are presented in Table 11.

- Replicates of reagent water procedure blanks were extracted for each sample set and when using new lots of extraction cartridges. The absence of absorption (versus another reagent water procedure blank) and the reproducibility of the UV spectra for these blanks were used to evaluate the effectiveness of the routine cartridge cleanup.

- All spike experiments were conducted in triplicate, and replicates of sample blanks were also prepared for each high and low spiking set for background evaluation and baseline determination.

TABLE 11. RESULTS OF DAILY QUALITY ASSURANCE ANALYSIS OF BENZENE STANDARDS BY UV SPECTROMETRY

Maximum Absorbance at 254 nm[a], a.u.												
Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Average	SD	RSD%
0.199	0.198	0.194	0.190	0.191	0.188	0.188	0.186	0.188	0.190	0.191	0.44	2

[a]All standards prepared at 75 µg/mL in methanol.

APPENDIX A

UV SPECTRA OF COMPOSITE GROUND-WATER
SPIKING EXPERIMENTS

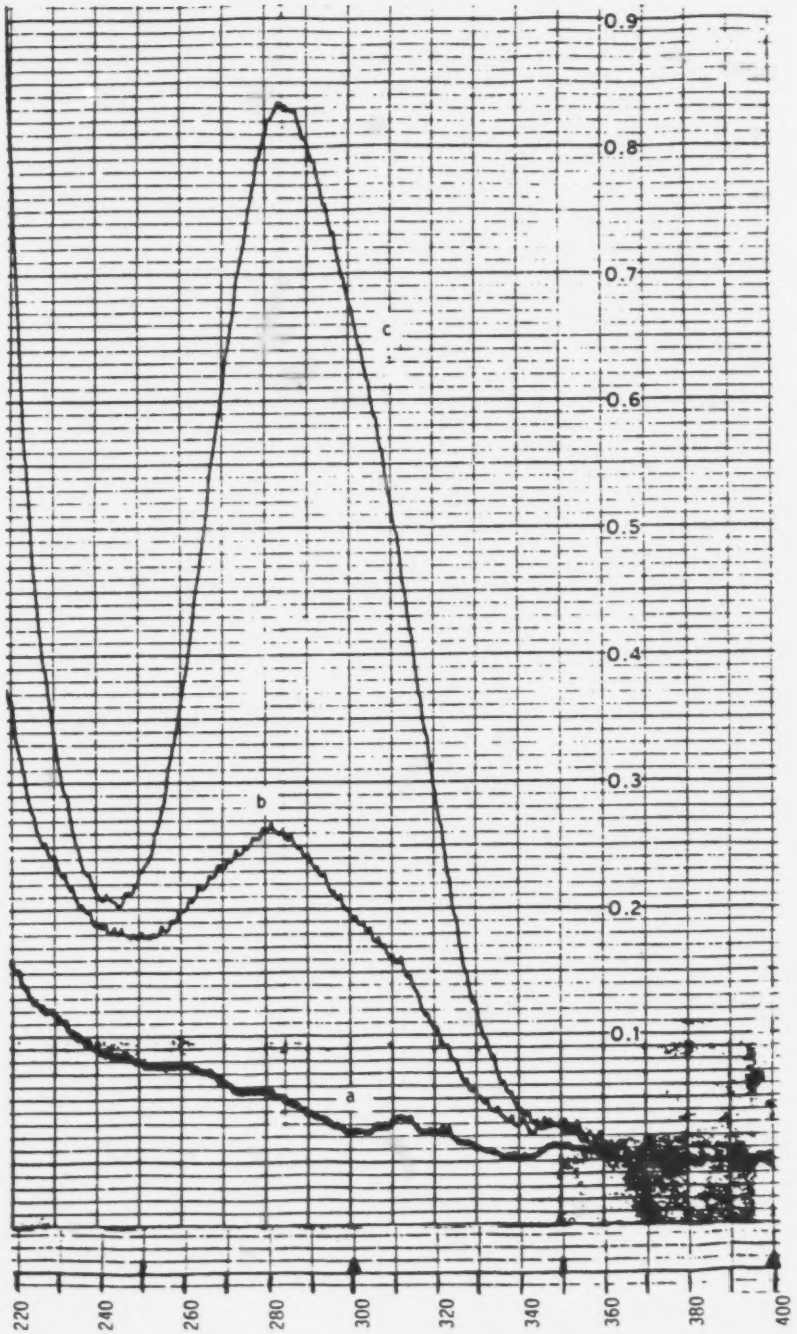


Figure A-1. UV spectra of (Rep 1) methanol eluents for 3,3'-dichlorobenzidine spiked composite ground water: spiking level (a) 0 µg/L (b) 20 µg/L (c) 100 µg/L

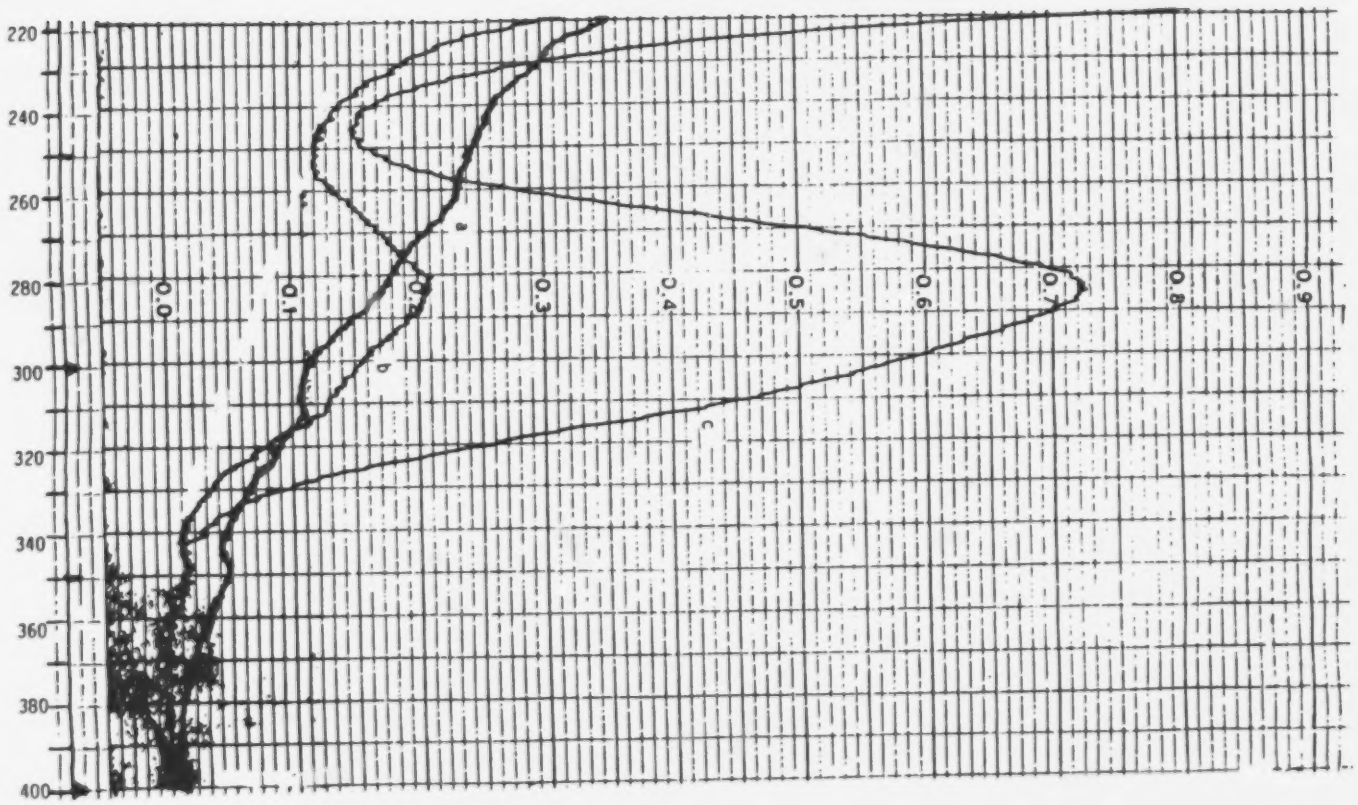


Figure A-2. UV spectra of (Rep 2) methanol eluents for 3,3'-dichlorobenzidine spiked composite ground water: spiking level (a) 0 µg/L (b) 20 µg/L (c) 100 µg/L

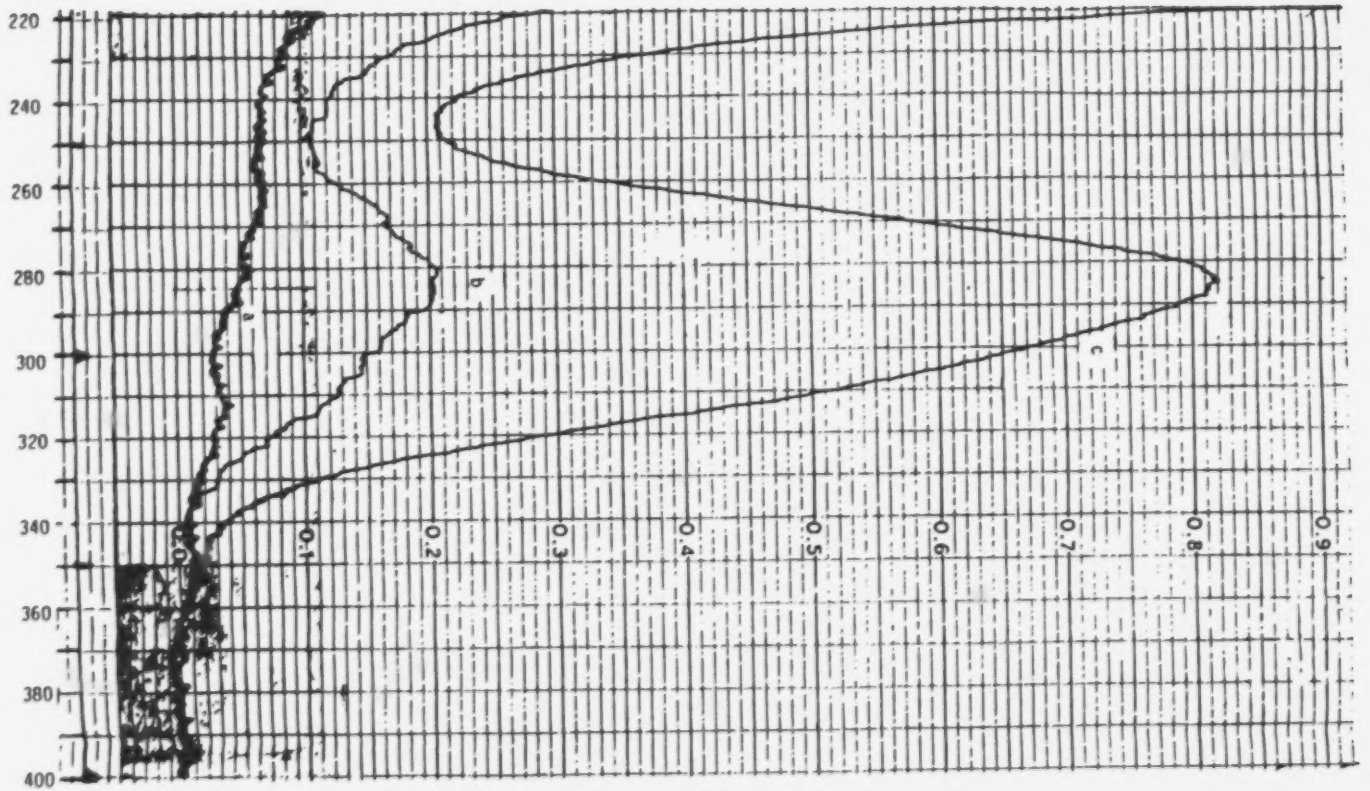


Figure A-3. UV spectra of (Rep 3) methanol eluents for 3,3'-dichlorobenzidine spiked composite ground water: spiking level (a) 0 µg/L (b) 20 µg/L (c) 100 µg/L

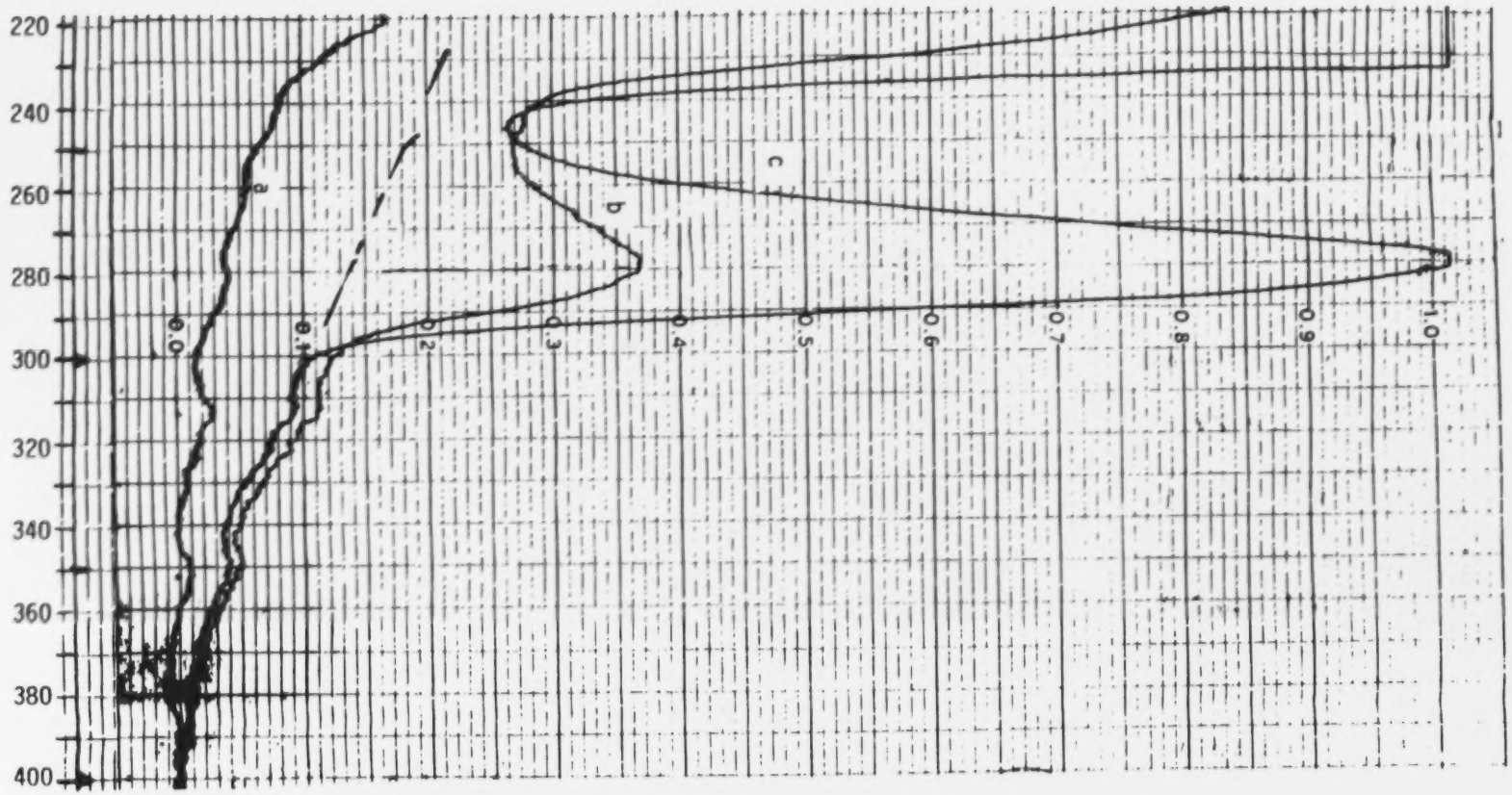


Figure A-4. UV spectra of (Rep 1) methanol eluents for 2,4-dimethylphenol spiked composite ground water: spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L

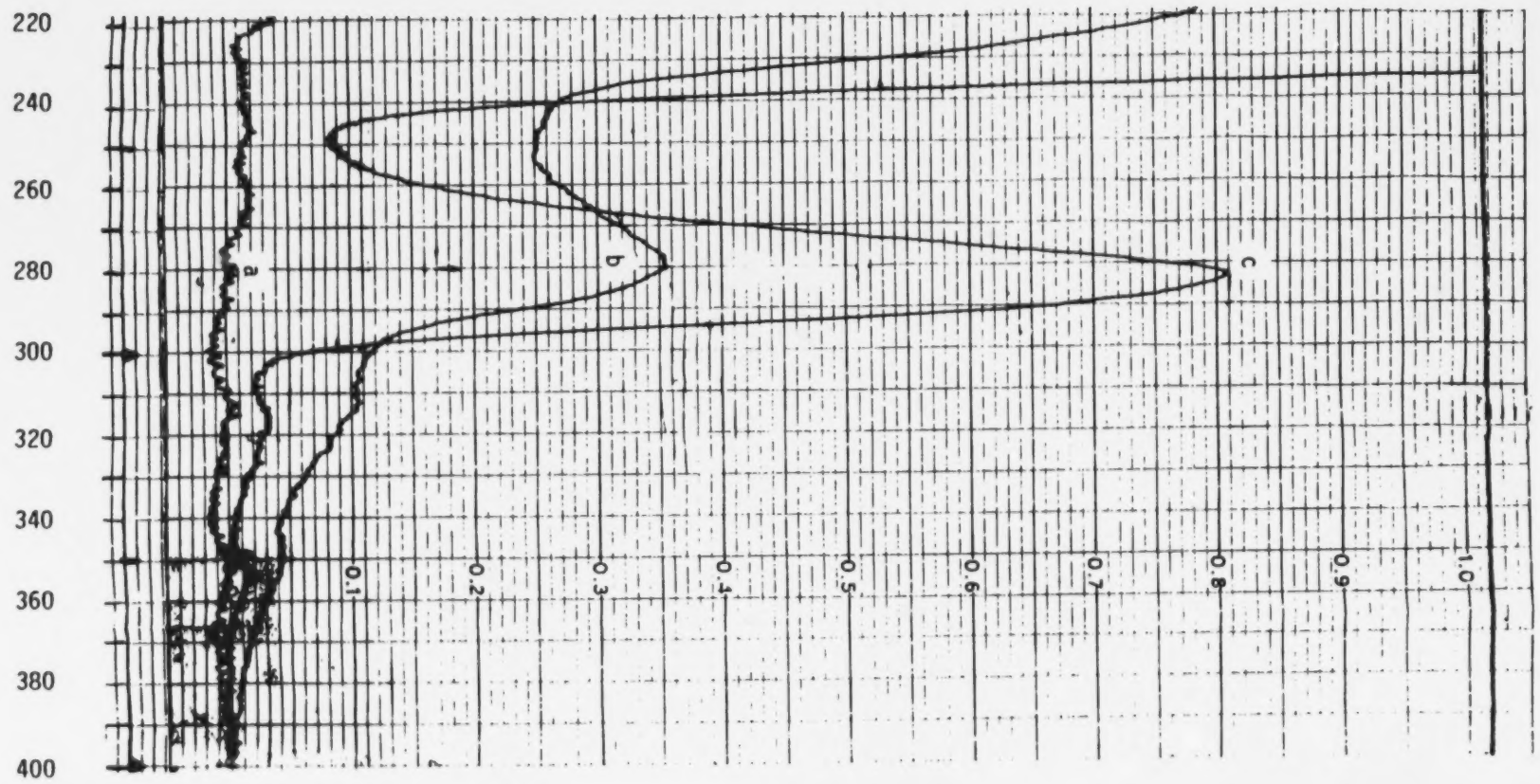


Figure A-5. UV spectra of (Rep 2) methanol eluents for 2,4-dimethylphenol spiked composite ground water: spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L

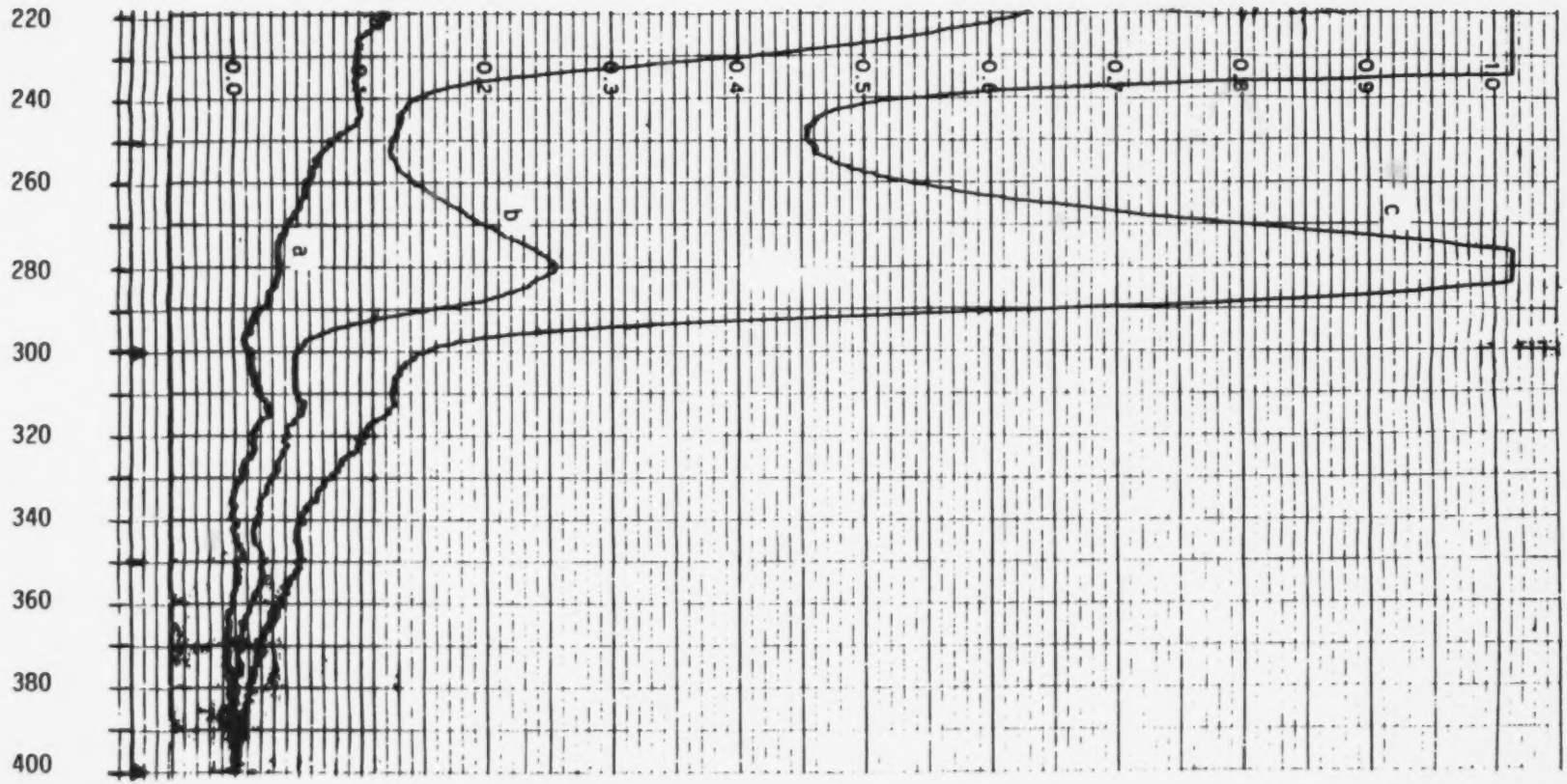


Figure A-6. UV spectra of (Rep 3) methanol eluents for 2,4-dimethylphenol spiked composite ground water: spiking level (a) 0 µg/L (b) 150 µg/L (c) 750 µg/L

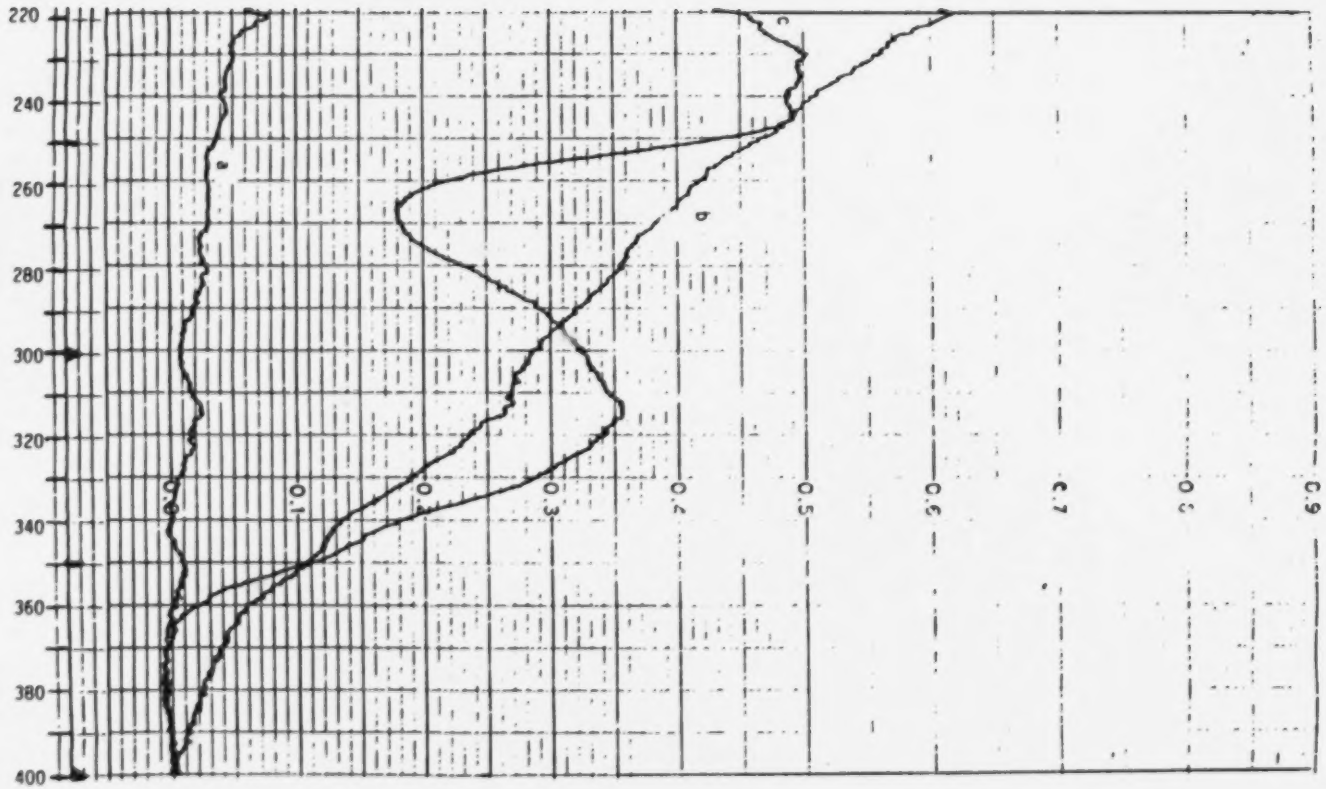


Figure A-7. UV spectra of (Rep 1) methanol eluents for 1,2-diphenylhydrazine spiked composite ground water: spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L

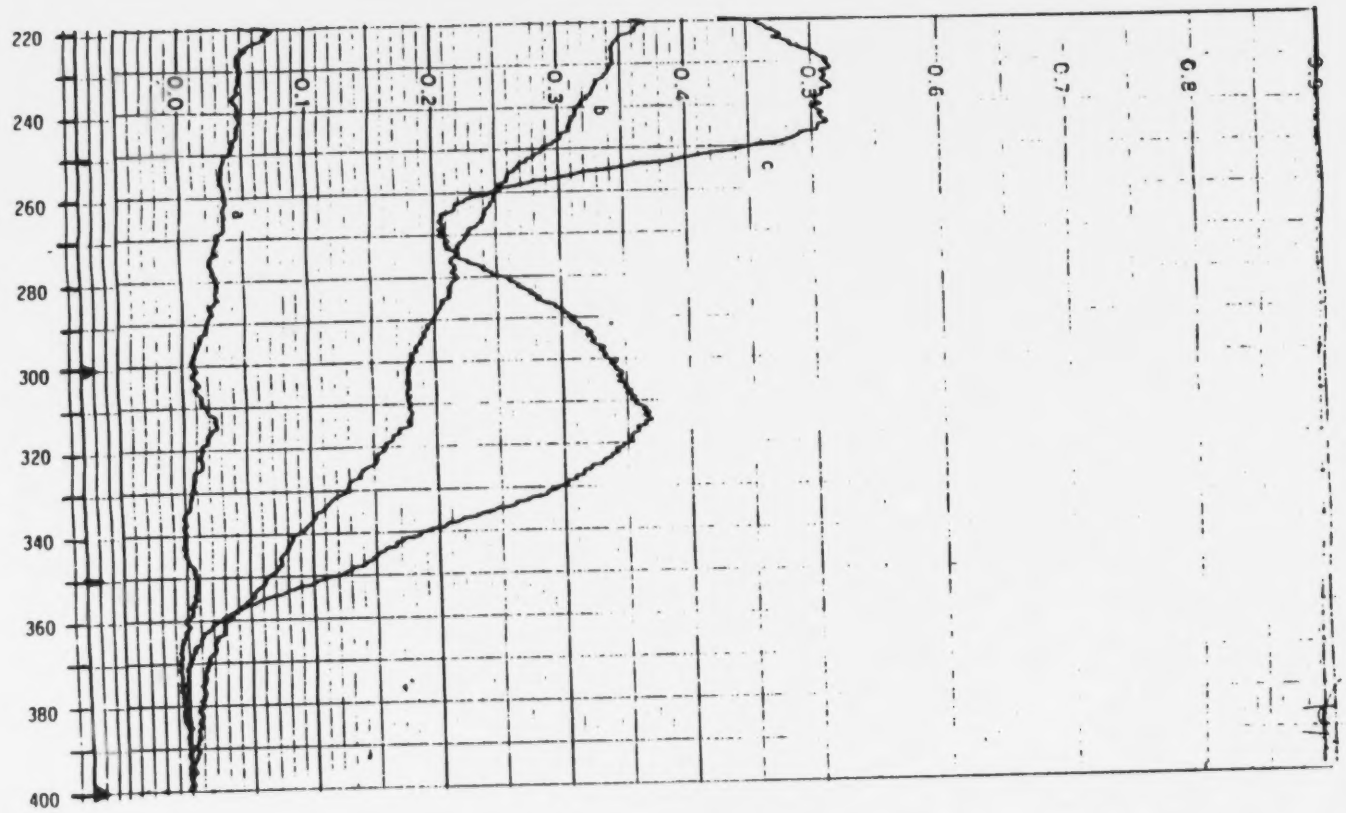


Figure A-8. UV spectra of (Rep 2) methanol eluents for 1,2-diphenylhydrazine spiked composite ground water: spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L

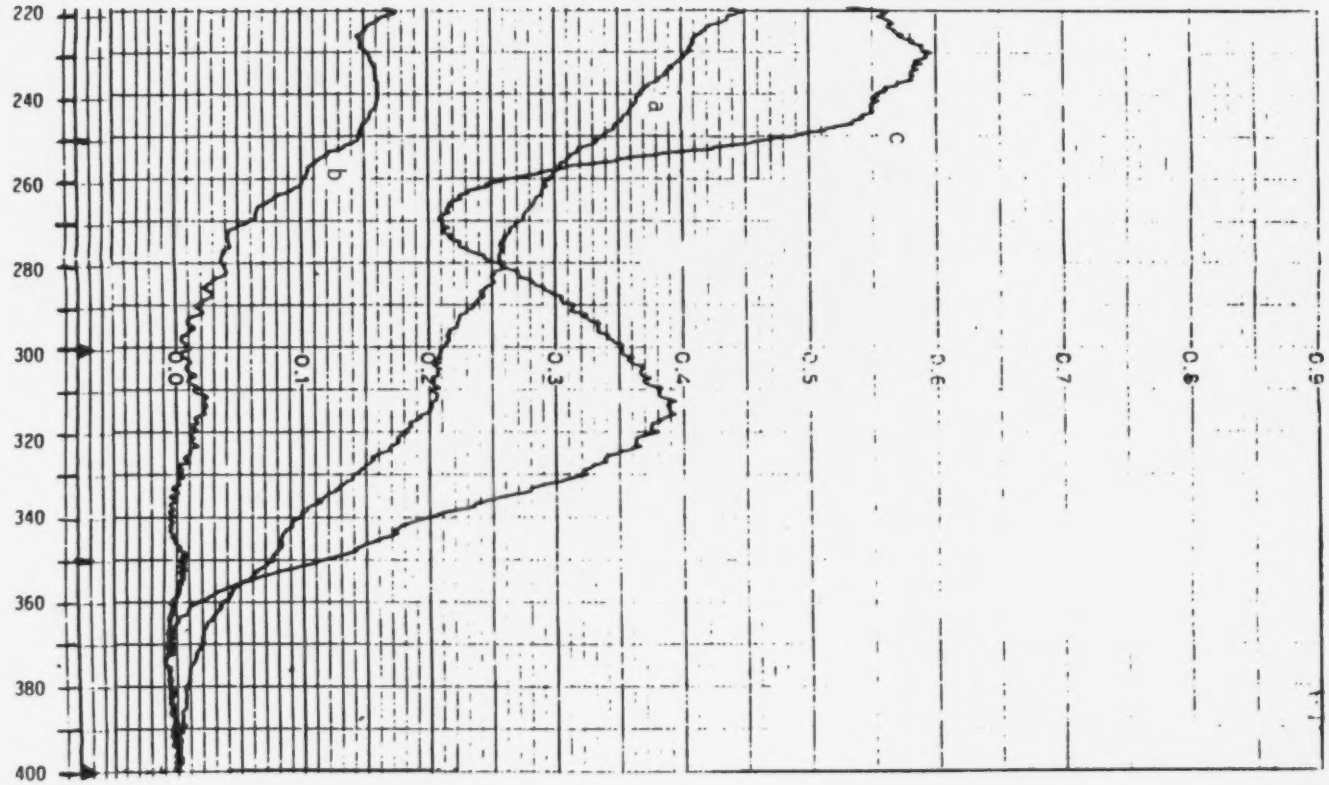


Figure A-9. UV spectra of (Rep 3) methanol eluents for 1,2-diphenylhydrazine spiked composite ground water: spiking level (a) 0 µg/L (b) 15 µg/L (c) 75 µg/L

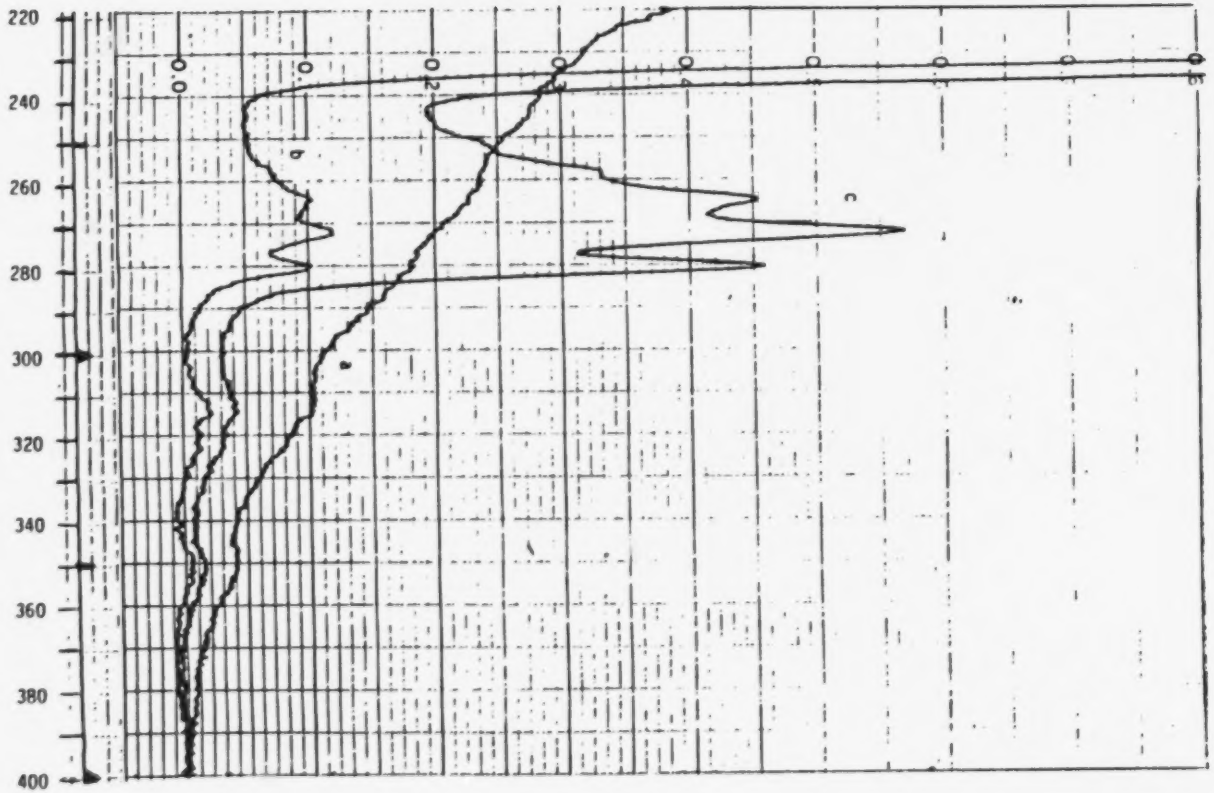


Figure A-10. UV spectra of (Rep 1) methanol eluents for 1,4-dichlorobenzene spiked composite ground water: spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L

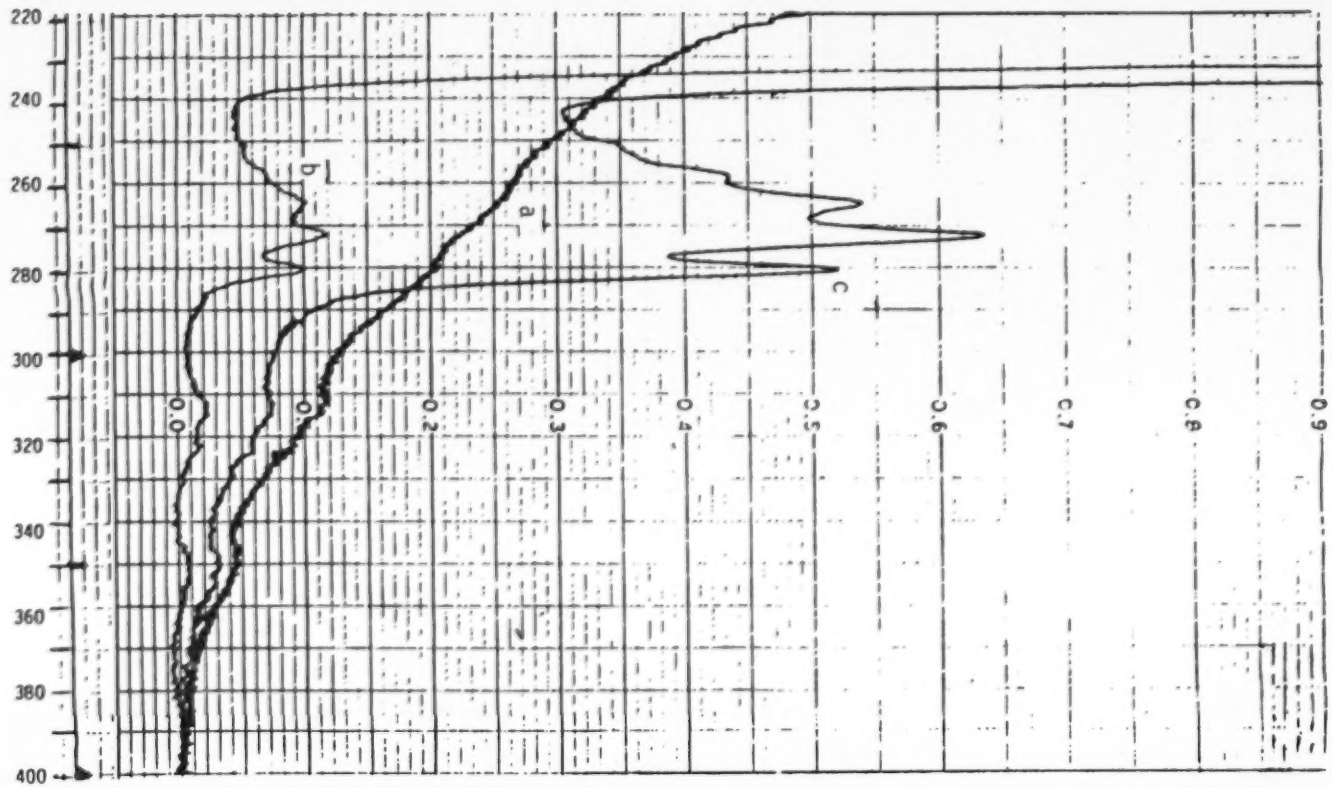


Figure A-11. UV spectra of (Rep 2) methanol eluents for 1,4-dichlorobenzene spiked composite ground water: spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L

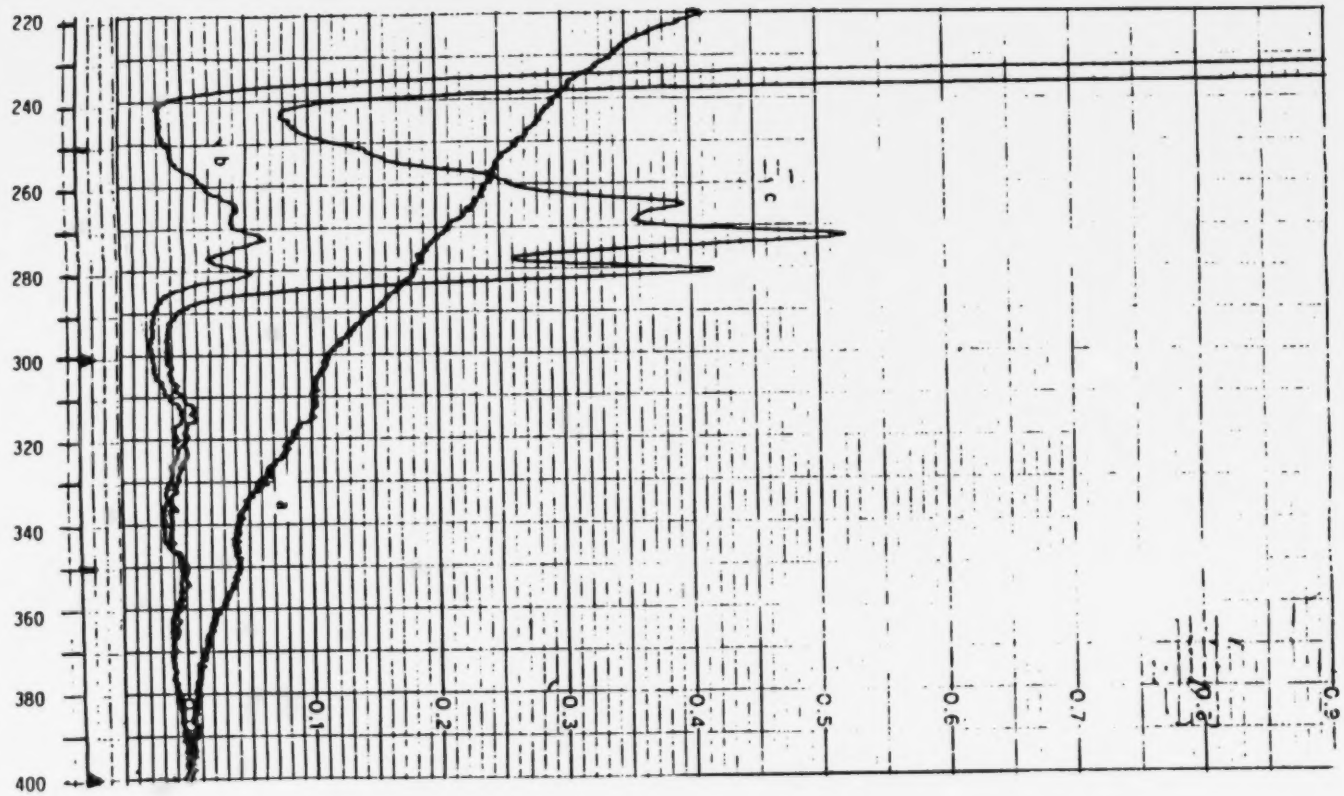


Figure A-12. UV spectra of (Rep 3) methanol eluents for 1,4-dichlorobenzene spiked composite ground water: spiking level (a) 0 µg/L (b) 600 µg/L (c) 3000 µg/L

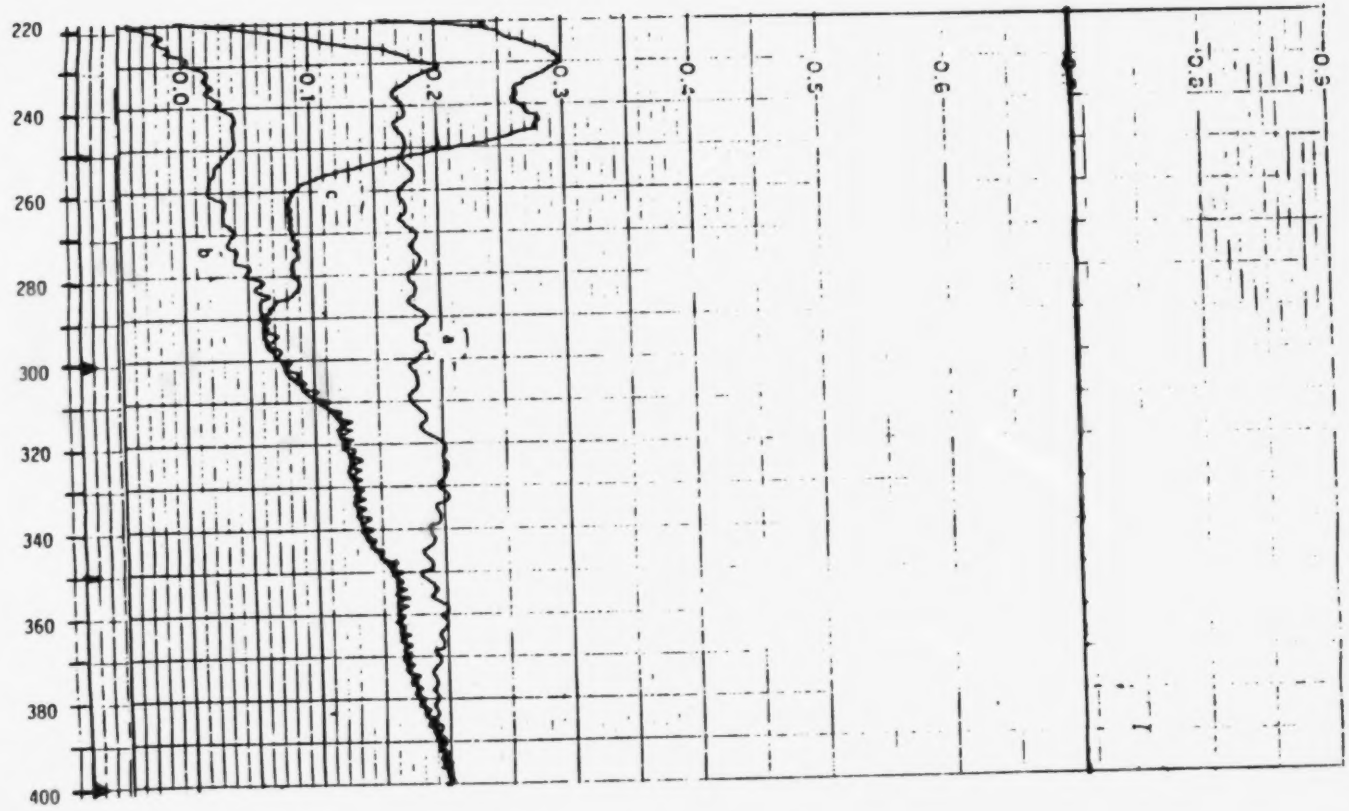


Figure A-13. UV spectra of (Rep 1) methanol eluents for methoxychlor spiked composite ground water: spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L (d) pseudo baseline.

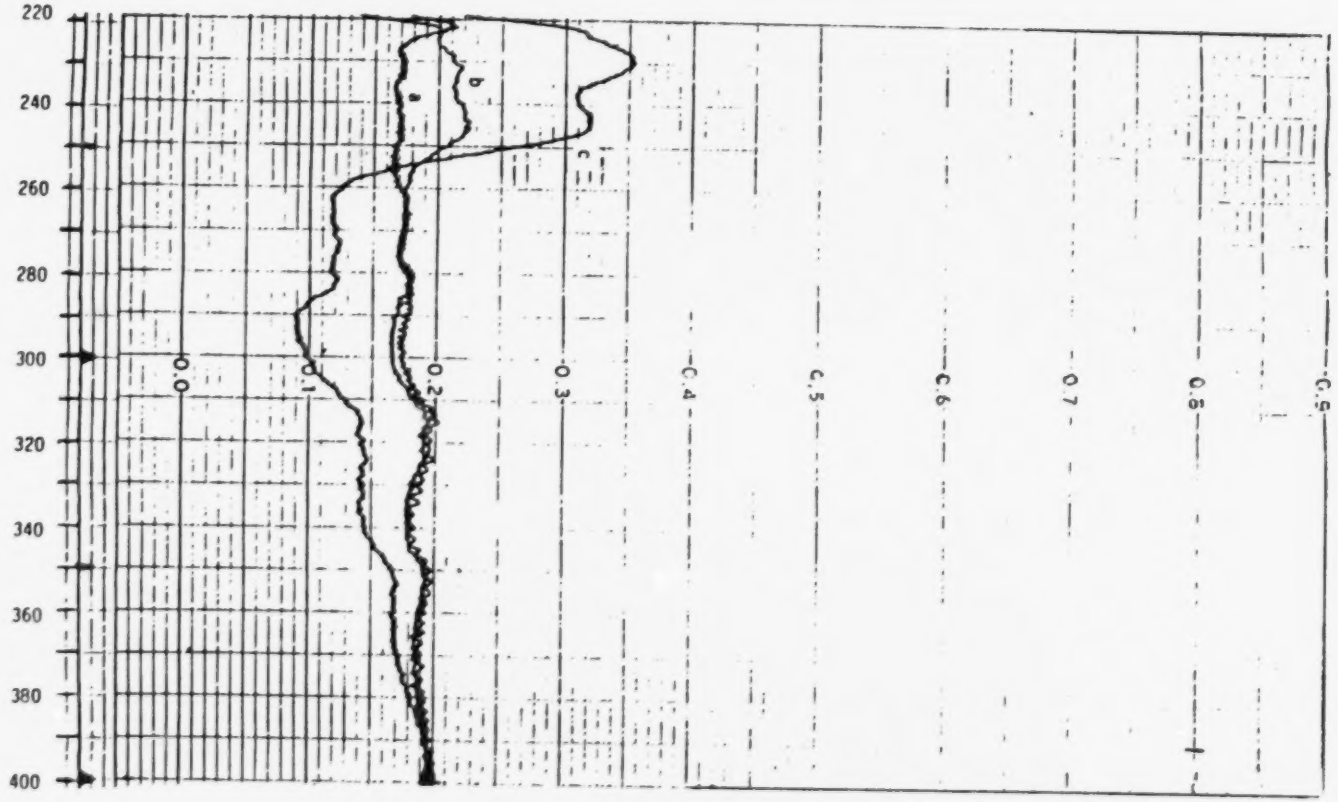


Figure A-14. UV spectra of (Rep 2) methanol eluents for methoxychlor spiked composite ground water: spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L

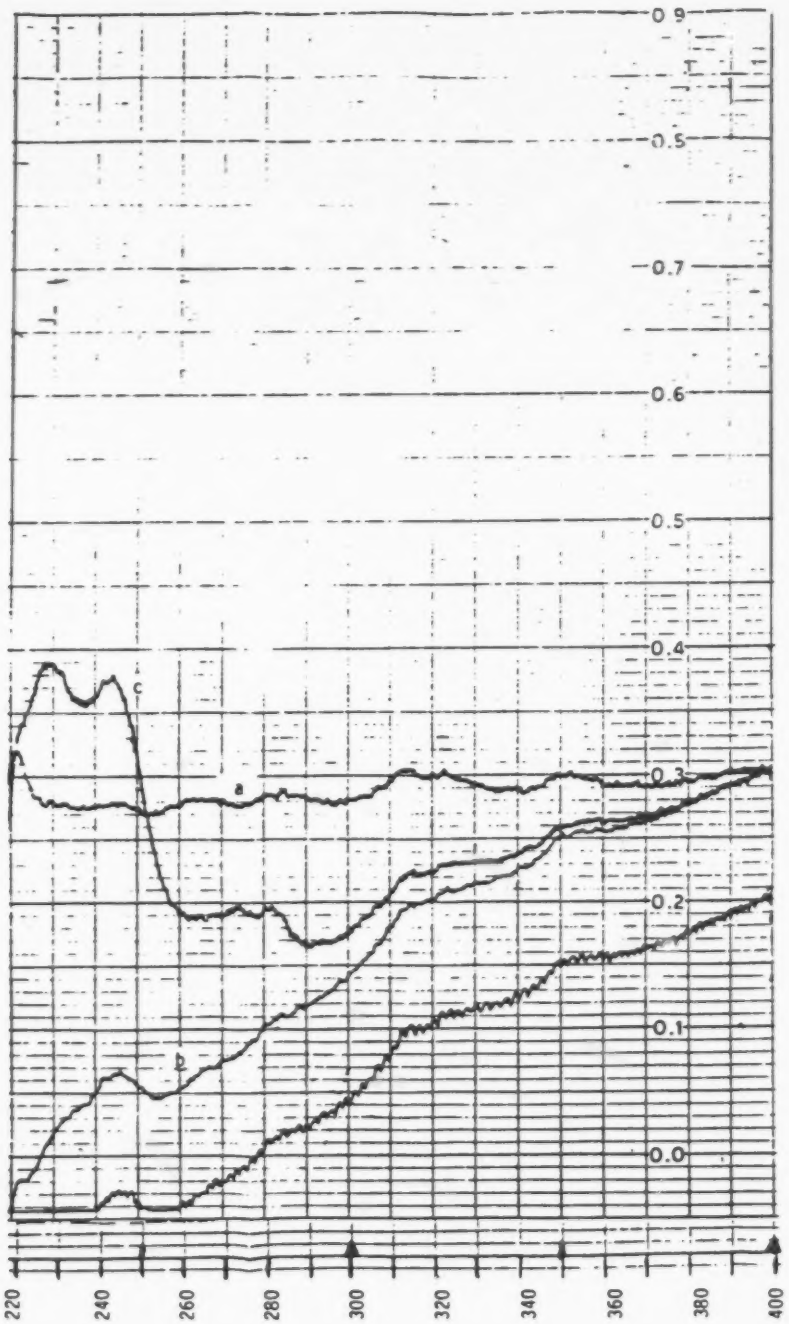


Figure A-15. UV spectra of (Rep 3) methanol eluents for methoxychlor spiked composite ground water: spiking level (a) 0 µg/L (b) 30 µg/L (c) 150 µg/L

TABLE B-1. DETECTION LIMIT ESTIMATION[a] FOR UV ACTIVE POLAR ORGANIC COMPOUNDS

ID#	Compound	Solvent	λ_{max}	Absorptivity at λ_{max} ($\log \varepsilon$)	EDL[b] µg/L	Reference[c]
1	Acetophenone	Methanol	240	7150(3.85)	16	R1-953
2	3-(alpha-Acetonylbenzyl)-4-hydroxycomarin	--	287	1120(3.05)	274	R8-C543
3	2-Acetylaminoflourene	Methanol/ Cyclohexane	314	30200(4.48)	8	R 7-18-411
4	4-Aminobiphenyl	Methanol	278	20500(4.3)	8	R1-18845
5	Mitomycin C	Methanol	357	22900(4.36)	14	R7-7-616
6	5-(Aminomethyl)-3-isoxazolol	--	--	--	--	--
7	Amitrole	Methanol	218	2190(3.34)	--	R7-13-3
8	Aniline	Methanol	230	8510(3.93)	10	R7-11-44
9	Aramite	Hexane	275	2.61(0.42)	127,000	RH-54(5)-1040
10	Auramine	Ethanol	425	6170(4.79)	4	R8-a1473
11	Benzenethiol	Methanol	266	501(2.70)	220	R7-13-48
12	Benzidine	Methanol	284	24500(4.39)	8	R1-6632
13	p-Benzoquinone	Ethanol	242	18200(4.26)	6	R-8-b206
14	N,N-Bis(2-chloroethyl)-2-napthylamine	Methanol	254	54700(4.73)	6	R2-1174-173,174
15	Bis(2-ethylhexyl) phthalate	Ethanol	224	7240(3.86)	--	R7-9-78
16	Brucine	Ethanol	301	8710(3.94)	46	R7-1-964
17	Butyl benzyl phthalate	Methanol	275	11700(4.07)	26	R12-50
18	2-sec-Butyl-2,4-dinitrophenol (DNBP)	Methanol	262, 370	8940(3.95), 11200(4.05)	26 21	R12-50

(continued)

TABLE B-1. (Continued)

ID#	Compound	Solvent	max	Absorptivity at max(log)	EDL[b] µg/L	Reference[c]
19	Chlorambucil	Methanol	259	19100(4.28)	16	R2-1501
20	p-Chloroaniline	Ethanol	242	7940(3.9)	16	R8-a1084
21	Chlorobenzilate	Ethanol	266	776(2.89)	418	
22	p-Chloro-m-cresol	Methanol	282	1940(3.29)	64	R1-1303
23	2-Chlorophenol	Cyclohexane	281	2440(3.39)	52	R1-2800
24	Citrus red No. 2	Ethanol	315 516	7590(3.88), 2090(4.32)	40, 14	R7-13-671
25	Coal tars	Methanol	250	1040(3.01)	10	R12-50
26	Creosote	Methanol	275	163(2.21)	61	R12-50
27	Cresols o-cresol m-cresol p-cresol	Methanol	272 273 279	1820(3.26) 1570(3.20) 1950(3.29)	60 68 56	R1-259 R1-2338 R1-33
28	2-Cyclohexyl-4,-dinitrophenol	--	--	--	--	--
29	Daunomycin	Methanol	232, 251	35000(4.54) 23800(4.38)	15, 22	R12-50
30	Diallate	Methanol	225	6030(3.78)	22	R12-50
31	Di-n-butyl phthalate	Ethanol	274	1230(3.09)	226	R7-2-701
32	3,3'-Dichlorobenzidine[d]	Ethanol	286	25200(4.4)	10	R7-2-295
33	2,4-Dichlorophenol	n.s.g.	286.3	2510(3.40)	64	R7-16-28
34	2,6-Dichlorophenol	Ethanol	290	2000(3.3)	82	R7-3-53
35	2,4-Dichlorophenoxyacetic acid	Methanol	252	400(2.60)	850	R1-13141
36	O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	Ethanol	274	8900(3.95)	256	R9-10-6893

(continued)

TABLE B-1. (Continued)

ID#	Compound	Solvent	λ max	Absorptivity at λ max(log ε)	EDL[b] ug/L	Reference[c]
37	Diethyl phthalate	Methanol	274.5	1270(3.10)	174	R1-375
38	Diethylstilbesterol	Methanol	239	17000(4.23)	16	R1-3889
39	Dihydrosafrole	Ethanol	287	3720(3.57)	44	R7-3-254
40	3,4-Dihydroxy- -(methyl-amino)methyl benzyl alcohol	Aqueous	290	794(2.90)	230	R8-C103
41	3,3'-Dimethoxybenzidine	Methanol	303	19600(4.29)	12	R1-1738
42	p-Dimethylaminoazobenzene	Benzene	253, 313	10400(4.02), 4080(3.61)	22, 56	R1-347
43	3,3'-Dimethylbenzidine	Methanol	282	23600(4.37)	10	R7-1-580
44	, -Dimethylphenethylamine	Cyclohexane	268	200(2.30)	744	R1-10948
45	2,4-Dimethylphenol[d]	Methanol	281	2140(3.33)	114	R7-11-112
46	Dimethyl phthalate	Ethanol	274	259(3.10)	154	R8-C436
47	Dinitrobenzenes,					
	o-Dinitrobenzene	Hexane	240	7600(3.88)	24	R2-555
	m-Dinitrobenzene	Methanol	233	18500(4.26)	10	R1-33
	p-Dinitrobenzene	Ethanol	266	14500(4.16)	12	R8-C164
48	4,6-Dinitro-o-cresol	Methanol	263	13900(4.14)	14	R1-10554
49	2,4-Dinitrophenol	Methanol	254	11500(4.06)	16	R1-11646
50	2,4-Dinitrotoluene	Cyclohexane	234	14000(4.14)	14	R1-9596
51	2,6-Dinitrotoluene	Methanol	232.5	9670(3.98)	18	R1-5514
52	Di-n-octyl phthalate	Cyclohexane	287	916(2.96)	426	R1-2906
53	Diphenylamine	Cyclohexane	282	8240(3.92)	20	R1-68 (continued)

TABLE B-1. (Continued)

ID#	Compound	Solvent	λ max	Absorptivity at λ max(log ε)	EDL[b] µg/L	Reference[c]
54	1,2-Diphenylhydrazine[d]	Ethanol	245, 290	20000(4.3), 4000(3.6)	10, 46	R8-C343
55	Isosafrole (cis)	96% Alcohol	259, 296	10000(4.0), 4450(2.65)	16, 30	R9-751 #5072
	(Trans)	96% Alcohol	259.5, 305	12200(4.08), 5340(3.73)	14 30	R9-751 #5072
56	Maleic hydrazide	Methanol	310	2500(3.40)	46	R1-7221
57	Methapyrilene	Ethanol	240, 305	17000(4.23) 4000(3.60)	16 66	R7-2-423
58	4,4'-Methylenebis-(2-chloroaniline)	Methanol	247	18600(4.27)	14	R1-10631
59	Methyl parathion	Methanol	271.5	7880(3.90)	34	R1-11044
60	1,4-Naphthoquinone	Ethanol	246, 334	19100(4.28), 2750(3.44)	8, 58	R7-15-186
61	1-Naphthylamine	Cyclohexane	243, 318	27700(4.44), 5100(3.71)	6 28	R1-9508
62	2-Naphthylamine	Cyclohexane	237, 280, 334	60000(4.78), 7020(3.85), 2330(3.37)	4 20, 62	R1-46
63	Nicotine	Cyclohexane	256	2450(3.38)	66	R1-1355
64	p-Nitroaniline	Methanol	228	2080(3.32)	--	R1-845
65	Nitrobenzene	Ethanol	260	8128(3.91)	16	R-8-C169
66	4-Nitrophenol	Methanol	311	11000(4.04)	12	R1-1684 (continued)

TABLE B-1. (Continued)

ID#	Compound	Solvent	λ max	Absorptivity at λ max(log ε)	EDL[b] µg/L	Reference[c]
67	Parathion	Ethanol	274	3980(3.6)	74	R7-1-348
68	Pentachloronitrobenzene (PCNB)	Cyclohexane	302	645(2.81)	458	R7-17-25
69	Pentachlorophenol	Methanol	273, 280	1050(3.02), 911(2.96)	254, 292	R1-112
70	Phenacetin	Methanol	249	10000(4.0)	18	R1-102
71	Phenylenediamine					
	o-Phenylenediamine	Methanol	237, 292	5860(3.77), 2920(3.46)	18, 38	R1-460
	m-Phenylenediamine	Methanol	294	2300(3.36)	48	R1-6522
	p-Phenylenediamine	Methanol	243	10000(4.0)	10	R7-16-39
72	N-Phenylthiourea	Methanol	264	12500(4.10)	12	R1-1273
73	Phosphorothioic acid, O,O-dimethyl O-(p((dimethyl-amino)-sulfonyl)phenyl) ester	Methanol	230	13400(4.13)	24	R12-50
74	Phthalic acid ester, N.O.S.					
	Benzylbutyl ester	(See #17)				
	Dibutyl ester	(See #31)				
	Diethyl ester	(See #37)				
	Dimethyl ester	(See #46)				
	Di-n-Octyl ester	(See #52)				
	Bis(2-ethylhexyl)phthalate	(See #15)				
75	Phthalic Anhydride	Methanol	274	1290(3.11)	114	R1-18
76	2-Picoline	Methanol	261	3887(3.59)	24	R1-9 (continued)

TABLE B-1. (Continued)

ID#	Compound	Solvent	max	Absorptivity at max(log)	EDL[b] ug/L	Reference[c]
77	Propylthiouracil	Methanol	276	15800(4.20)	10	R7-4-131
78	Pyridine	Methanol	256.5	2480(3.39)	32	R1-15
79	Reserpine	Methanol	267	17000(4.23)	36	R7-2-842
80	Resorcinol	Methanol	275	2110(3.32)	52	R1-9700
81	Safrole	Ethanol	236, 285	4170(3.62), 3800(3.58)	38, 42	R7-3-243
82	Strychnine	Ethanol	254, 278	12900(4.11), 4170(3.62)	26, 80	R7-9-694
83	Thioacetamide	Ethanol	266	12600(4.10)	6	R7-17-2
84	2,4,5-Trichlorophenol	Methanol	292.5	2850(3.45)	8	R1-14019
85	2,4,6-Trichlorophenol	Aqueous	286	2240(3.35)	88	R7-13-38
86	2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	Methanol	288.5, 296.5	2530(3.40), 2330(3.37)	100, 110	R1-3432
87	2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP) (D)	Methanol	288	2370(3.37)	114	R1-10914
	(L)	Methanol	288.5	2420(3.38)	112	R1-10915
88	sym-Trinitrobenzene	Methanol	330	316(2.5)	674	R8-6981
89	Trypan blue	--	--	--	--	--
90	Uracil mustard	5% Ethanol	757	5680(3.75)	44	R9-10-1264

[a]Based on a recovery of 100 and a concentration factor of 20 for Method 3560.

[b]EDL = Estimated Detection Limit (for UV/visible Range 230-400 nm).

[c]Selected references from data base (Table 4 and 5) compiled in Phase 1, Final Report.

[d]Compounds selected for matrix spiking study.

TABLE B-2. DETECTION LIMIT ESTIMATION[a] FOR UV ACTIVE NONPOLAR ORGANIC COMPOUNDS

ID#	Compound	Solvent	λ max	Absorptivity at λ max(log ξ)	EDL[b] µg/L	Reference[c]
1	Benz(c)acridine	Methanol	274	57300(4.76)	4	R1-19734
2	Benz(a)anthracene	Methanol	288	90200(4.96)	2	R1-1124
3	Benzene	Cyclohexane	254	212(2.33)	368	R1-579
4	Benzene, dichloromethyl	Isooctane	265	449(2.65)	358	R1-2489
5	Benzo(b)fluoranthene	Ethanol	256, 428	70800(4.85), 8320(3.92)	4, 30	R-4-794
6	Benzo(j)fluoranthene	Ethanol	310	36300(4.56)	8	R7-18-652
7	Benzo(a)pyrene	Ethanol/Cyclohexane	266, 364	25100(4.40), 20000(4.30)	10, 12	R7-4-794
8	Benzotrichloride	Methanol	267	558(2.75)	350	R1-380
9	-Chlorotoluene	Methanol	259	231(2.36)	548	R1-5
10	4-Bromophenylphenylether	Cyclohexane	235	16800(4.22)	14	R1-2269
11	Chlorinated benzene					
	Chlorobenzene	Methanol	264	190(2.28)	590	R7-4-59
	1,2-Dichlorobenzene	(See #24)				
	1,3-Dichlorobenzene	(See #25)				
	1,4-Dichlorobenzene	(See #26)				
	1,2,3-trichlorobenzene	Methanol	271	178(2.25)	1020	R1-1673
	1,2,4-Trichlorobenzene	Methanol	277	482(2.68)	376	R1-1277
	1,3,5-Trichlorobenzene	Ethanol	273	234(2.37)	774	R7-4-57
	1,2,3,4-Tetrachlorobenzene	Cyclohexane	281	294(2.47)	734	R1-5935
	1,2,3,5-Tetrachlorobenzene	Ethanol/Hexane	281	316(2.50)	680	R7-4-49
	1,2,4,5-Tetrachlorobenzene	Cyclohexane	231,	11700(4.07),	18,	R1-2976
		Ethanol/Hexane	285	1050(3.02)	206	R7-4-49
	Pentachlorobenzene	Ethanol/Hexane	288	407(2.61)	614	R7-9-30

(continued)

TABLE B-2. (Continued)

ID#	Compound	Solvent	max	Absorptivity at max (log)	EDL[b] µg/L	Reference[c]
	Hexachlorobenzene	Ethanol	291	245(2.39)	1160	R7-5-44
12	2-Chloronaphthalene	Methanol	288	2950(3.47)	56	R7-4-254
13	Chrysene	Cyclohexane Ethanol	258, 267	91200(4.96), 159000(5.20)	2, 2	R7-2-546
14	DDD	Methanol	231	19400(4.29)	16	R1-18450
15	DDE	Ethanol	245	17400(4.24)	18	R7-14-375
16	DDT	Methanol	240	19900(4.30)	16	R1-15542
17	Dibenz(ah)acridine	Ethanol	312	12020(4.08)	24	R7-1-888
18	Dibenz(aj)acridine	Ethanol	290	64600(4.81)	4	R-6-549
19	Dibenz(ah)anthracene	Methanol	300	126000(5.1)	2	R7-4-882
20	7H-Dibenzo(cg)carbazole	Ethanol	288	53700(4.73)	6	R7-16-681
21	Dibenzo(ae)pyrene	Benzene	306	63100(4.8)	4	R7-1-975
22	Dibenzo(ah)pyrene	Benzene Ethanol	313 256	158000(5.2) 63100(4.8)	2 4	R6-51 R7-1-975
23	Dibenzo(ai)pyrene	Ethanol	242	100000(5.0)	1	R7-1-975
24	o-Dichlorobenzene	Isooctane	269	329(2.52)	446	R1-1003
25	m-Dichlorobenzene	Methanol				
26	p-Dichlorobenzene[d]	Methanol	271	377(2.58)	390	R1-55
27	Dichlorobenzene (N.O.S.)	(See #11)				
28	7,12-Dimethylbenz(a)-anthracene	Methanol	295	90100(4.96)	2	R1-9270

(continued)

TABLE B-2. (Continued)

ID#	Compound	Solvent	λ max	Absorptivity at λ max(log ξ)	EDL[b] µg/L	Reference[c]
29	Fluoranthene	Ethanol	236 287	45700(4.66), 45700(4.66)	4 4	R7-17-452
30	Heptachlor	Ethanol	236 309	60300(4.78), 9120(3.96)	6, 40	R-8-d165
31	Hexachloro-1,3-butadiene	Methanol	249	4390(3.64)	60	R1-3229
32	Hexachlorocyclopentadiene	Methanol	321	1480(3.17)	184	R1-1397
33	Hexachlorophene	Methanol	299	6020(3.78)	68	R1-1576
34	Indeno(1,2,3-cd)pyrene	Methanol	249	82600(4.92)	338	R1-11202
35	Methoxychlor[d]	Methanol	244	13100(4.12)	26	R1-17345
36	Methylcholanthrene	Ethanol	297	79400(4.90)	4	R7-1-892
37	Naphthalene	Methanol	275	5530(3.74)	24	R1-265
38	Polychlorinated biphenyls (N.O.S.) Arochlor 1242	Methanol	244	363(2.56)	551	R12-50
39	TCDD	Chloroform	306	6030(3.78)	54	R7-16-249

[a]Based on a percent recovery of 100 and a concentration factor of 20 for Method 3560.

[b]EDL = Estimated Detection Limit for UV/visible Range 230-400 nm.

[c]Selected references from data base (Table 4 and 5) compiled in Phase 1 Final Report.

[d]Compounds selected for matrix spiking study.

APPENDIX C

U.S. EPA METHOD 8610

TOTAL AROMATICS BY ULTRAVIOLET ABSORPTION

1.0 Scope and Application

1.1 Method 8610 is designed to measure total aromatics present in extracts of groundwater samples by measuring the UV absorption of the sample relative to a background sample or a method blank. This method may be used with extracts of groundwater prepared by Method 3560.

1.2 Method 8610 is a screening method that may only be applied to groundwater samples as provided in Method 8600. The UV screening of groundwater samples is a simple, sensitive, and inexpensive method of determining which Appendix VIII compounds may be present in the sample.

1.3 This method may be used to determine the absence of the following compounds:

Polar UV Compounds

Acetophenone
3-(alpha-Acetonylbenzyl)-4-hydroxycomarin, and salts
2-Acetylaminoflourene
4-Aminobiphenyl
Mitomycin C
5-(Aminomethyl)-3-isoxazolol
Amitrole
Aniline
Aramite
Auramine
Benzenethiol
Benzidine
p-Benzoquinone
N,N-Bis(2-chloroethyl)-2-napthylamine
Bis(2-ethylhexyl) phthalate
Brucine
Butyl benzyl phthalate
2-sec-Butyl-2,4-dinitrophenol (DNBP)
Chlorambucil
p-Chloroaniline
Chlorobenzilate
p-Chloro-m-cresol
2-Chlorophenol
Citrus red No. 2
Coal tars
Creosote
Cresols

2-Cyclohexyl-4,-dinitrophenol
Daunomycin
Diallate
Di-n-butyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dichlorophenoxyacetic acid, salts and esters (2,4-D)
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester
Diethyl phthalate
Diethylstilbesterol
Dihydrosafrole
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol
3,3'-Dimethoxybenzidine
p-Dimethylaminoazobenzene
3,3'-Dimethylbenzidine
alpha,alpha-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethyl phthalate
Dinitrobenzene, N.O.S.
4,6-Dinitro-o-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
Diphenylamine
1,2-Diphenylhydrazine
Isosafrole
Maleic hydrazide
Methapyrilene
4,4'-Methylenebis(2-chloroaniline)
Methyl parathion
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
Nicotine and salts
p-Nitroaniline
Nitrobenzine
4-Nitrophenol
Parathion
Pentachloronitrobenzene (PCNB)
Pentachlorophenol
Phenacetin
Phenylenediamine
N-Phenylthiourea
Phosphorothioic acid, O,O-dimethyl O-(p((dimethylamino)-sulfonyl)phenyl)
ester
Phthalic acid ester, N.O.S.
Phthalic anhydride

2-Picoline
Propylthiouracil
Pyridine
Reserpine
Resorcinol
Safrole
Strychnine and salts
Thioacetamide
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)
sym-Trinitrobenzene
Trypan blue
Uracil mustard

Non-Polar UV Compounds

Benz(c)acridine
Benz(a)anthracene
Benzene
Benzene, dichloromethyl-
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(a)pyrene
Benzotrichloride
Benzyl chloride
4-Bromophenyl phenyl ether
Chlorinated benzenes, N.O.S.
2-Chloronaphthalene
Chrysene
DDD
DDE
DDT
Dibenz(a,h)acridine
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
7H-Dibenzo(c,g)carbazole
Dibenzo(a,e)pyrene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
Dichlorobenzene, N.O.S.
7,12-Dimethylbenz(a)anthracene

Fluoranthene
Heptachlor
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachlorophene
Idenol(1,2,3-cd)pyrene
Methoxychlor
3-Methylcholanthrene
Naphthalene
Polychlorinated biphenyls, N.O.S.
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

2.0 Summary of Method

2.1 The extracted groundwater sample is reduced (or made up) to a volume of 1 ml and transfered to a quartz cuvette.

2.2 A reagent blank or an upgradient groundwater sample is extracted with the sample and the UV region, 310 nm to 220 nm, is scanned for each sample versus the reagent blank or the upgradient sample.

Note: This Method can also be used over a wide range. If compounds which absorb in the visable range are expected the scan range should be extended to 700 nm to 220 nm.

3.0 Interferences

3.1 A procedural blank should be performed prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

4.0 Apparatus and Materials

4.1 Quartz cuvettes, with a 1 cm path length. Cuvettes with a 1 cc volume are recommended.

4.2 Double beam, adjustable slit, UV/VIS spectrophotometer capable of scanning the range 700 nm to 220 nm with a recording device.

4.3 Disposable pipets.

5.0 Reagents

5.1 Methanol: ACS spectrophotometric grade.

5.2 Hexane: ACS spectrophotometric grade.

6.0 Sample Collection and Preservation

6.1 Since this method may destroy some compounds in the sample, subsequent analysis should be performed on a fresh sample aliquot.

6.2 If the sample will be analyzed by additional methods the sample should be stored at 4°C prior to any additional analyses. Samples should be completely analyzed within 4 weeks of extraction.

7.0 Procedures

7.1 Place the groundwater extract into the quartz cuvette. The sample volume may be adjusted by either reducing the volume under a stream of nitrogen or increasing the volume with either hexane or methanol (use whichever is appropriate depending upon the fraction being analyzed).

7.2 Place the upgradient groundwater extract (or the method blank) into another quartz cuvette using the same procedure as in 7.1.

7.3 Place the upgradient (or method blank) sample into the reference sample holder of the UV spectrophotometer and place the sample (downgradient) into the test sample holder.

7.4 Scan the spectrophotometer in the constant intensity (variable slit mode) over the range of 310 nm to 220 nm and record the results. The scan should take at least 1 min.

7.5 After the scan is complete place the sample extract back into the sample vial it was taken from. Rinse the cuvette twice with a small amount of the solvent used and add the rinses to the sample vial.

7.6 Repeat steps 7.1 through 7.5 for the other (polar or non-polar) extract.

8.0 Quality Control

8.1 Analyze the spiked duplicates and the spiked reagent blanks to verify the sensitivity and detection limits.

8.2 The spiked samples should yield an absorbance of about .005 (99% transmittance) in the range of 270 to 300 nm.

9.0 Detection Limits

9.1 The detection limits for the spiked compounds are as follows:

Floranthene	0.3 ppb
Parathion	4.0 ppb
Trichlorophenol	4.0 ppb

9.2 Detection limits for Appendix VIII compounds will vary depending on molar absorbtivity coefficiences. For example, the spiked reagent blank will contain 25 ng of Floranthene in 1 ml of hexane (λ_{max} = 286 nm; Σ = 45000). Therefore the absorbance will be

$$A = \frac{45000\,\lambda}{\text{cin-mole}}\ 1\text{ cm} \cdot 1.24 \times 10^{-7}\text{ moles/liter}$$

$$A = .0056$$

The cut-off used in deciding whether a compound was UV active was molar absorbtivity coefficient of 1000 or higher. Therefore a compound with a molecular wt of 250 gm/mole can first be detected at a level of:

$$.005 = \frac{1000\ 1}{\text{cin-mole}}\ 1\text{ cm} \times \text{moles/liter}$$

$$x = 5 \times 10^{-6}\text{ mole/l}$$

$$5 \times 10^{6}\text{ moles/l} \cdot 250\text{ gm/mole} = 1250 \times 10^{-6}\text{ gm/liter}$$

$$= 1.25\text{ mg/l}$$

Since we concentrated the sample 100:1 the detection limit of this method should be at least 12.5 ppb for all of the compounds listed.

10.0 Pass/Fail Criteria

10.1 The Pass/Fail criteria for groundwater samples determined using method 8610 is straight forward and utilizes the background correction supplied by the upgradient sample.

10.2 Since the up gradient sample is placed in the reference cell any absorption due to indigenous UV active compounds should be automatically subtracted out.

10.3 A ground water sample will fail method 8610 if the sample absorbs more than .005 absorbance units in the range from 310 nm to 220 nm.

APPENDIX D

U.S. EPA METHOD 3560

REVERSE PHASE CARTRIDGE EXTRACTION

1.0 Scope and Application

1.1 Method 3560 is designed to quantitatively extract non-purgeable organic compounds from groundwater samples using reverse phase concentration cartridges. This method is available as an alternative to Methods 3510, 3520, and 3530 for groundwater screening as described in Method 8600.

1.2 Method 3560 is advantageous compared to the other extraction methods since it is simple and effective and requires a minimum of sample preparation.

2.0 Summary of Method

2.1 The groundwater sample is drawn up into a 50-ml syringe and a pre-cleaned RP cartridge is fitted on the syringe. The sample is forced through the cartridge. This process is repeated with an additional 50 ml of sample.

2.2 The cartridge is washed with distilled water and then eluted either sequentially (for compound fractionation) or entirely with appropriate solvents.

3.0 Interferences

3.1 A procedural blank should be performed prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the sample.

4.0 Apparatus and Materials

4.1 Reverse phase C18 cartridges; (Water Sep Pac™, Analabs, or equivalent).

4.2 Glass Hypodermic Syringe; 50cc or larger.

4.3 Vials, 12 ml, borosolicate glass with Teflon Lined screw caps.

4.4 Distilled, deionized water.

4.5 Evaporation system (Pierce, Reacti-Therm™ system, or equivalent).

5.0 Reagents

5.1 Methanol: ACS reagent grade.

5.2 Hexane: ACS reagent grade.

6.0 Sample Collection, Preservation, Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation and handling.

6.2 After extraction of samples by this method, hexane and methanol extracts may be stored at 4°C prior to analysis. Sample extracts should be analyzed as soon as possible after extraction and should not exceed 4 weeks after extraction.

7.0 Procedure

7.1 Fill syringe with 5 ml methanol.

7.2 Attach reverse phase cartridge to the syringe and push the methanol through taking 1 min or more to completely empty the syringe.

7.3 Remove the cartridge and fill the syringe with 5 to 10 ml of distilled water.

7.4 Attach the cartridge and force the water through as before.

7.5 Remove the cartridge and fill the syringe with 50 ml of the sample groundwater.

7.6 Attach the cartridge and force the water sample through the cartridge at a rate of about 10 ml/min.

7.7 Repeat steps 7.5 and 7.6 with an additional 50 ml of sample.

7.8 Remove the cartridge and fill the syringe with 5 ml of distilled water. Attach the cartridge and force the distilled water through the cartridge as before.

7.9 Remove the cartridge and fill the syringe with 5-7 ml of hexane.

7.10 Attach the cartridge and force the hexane through 5 ml/min. Collect the hexane in a 12 ml vial.

7.11 At this point the sample volume should be reduced using an evaporation system that uses a stream of nitrogen and low heat (40-50°C). The sample volume should be reduced to ~.5 ml and made up to 1 ml with fresh hexane.

7.12 If the sample will not be analyzed immediately it should be sealed with a Teflon-lined cap and stored at 4°C until analysis.

7.13 Repeat steps 7.9 through 7.12 using methanol as the eluting solvent.

8.0 Quality Control

8.1 Every 10th sample or at least one sample in each set of samples should be a spiked duplicate. The sample should be spiked with 25 ng of fluoranthene, 0.4 µg of parathion and 0.4 µg 2,4,5 trichlorophenol.

8.2 Every 10th sample or at least one sample in each set of samples should be a spiked reagent blank. A 100-ml sample of distilled water should be spiked with 25 ng of fluoranthene, 0.4 µg of parathion and 0.4 µg of 2,4,5 trichlorophenol.

8.3 A reagent blank (i.e., distilled deionized water) should be run with each set of samples. This blank will be used to determine whether interfering compounds have been introduced during sample preparation.